

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN ordinary meeting of the Society was held on Wednesday evening, May 3, in the Chemical Society's Rooms, Burlington House. The President, Mr. G. Embrey, F.I.C., occupied the chair.

The minutes of the previous ordinary meeting were read and confirmed.

Mr. M. S. Salamon, B.Sc., was elected a member of the Society.

The following papers were read: "Excretion and Secretion of Salvarsan and Neo-Salvarsan," by John Webster, F.I.C.; and "Microscopical Methods," by H. G. Greenish, F.I.C.



THE MANUFACTURE OF CHEMICAL FILTER-PAPER.

By E. J. BEVAN, F.I.C., AND W. BACON, B.Sc., F.I.C.

(Read at the Meeting, March 1, 1916.)

PRIOR to the war the manufacture of filter-paper in England (suitable for quantitative work) had not been carried out, for various reasons. Of these, the more prominent were—Firstly, a shrinking from any new project requiring work and research; secondly, manufacturers were uncertain of support from users of such a commodity in this country sufficient to justify the expenditure involved in a new departure.

One firm in this country had for many years made a cheap filter-paper, excellent for qualitative work. But this paper could not fulfil the requirements of analytical work, and the standard of quality would have to be raised to meet such demands for papers outside the important range of acid-extracted paper.

We have endeavoured to get some idea of the total imports and consumption of filter-paper in this country, but unfortunately the Board of Trade in its returns makes

no specific reference to filter-paper, but includes it under the general heading of "various papers." If £10,000 per annum be assumed as representing the total value of paper cut in circles imported to the United Kingdom, then, taking an average size of 12·5 cms., and a weight of a quarter of a pound per 100 circles, and a cost of 4s. per pound, this to include the ashless type, we should get a figure approximating to 2,000,000 circles yearly. To this must be added the large amount of filter-paper imported in sheet form by large users, a quantity probably ten times as much as that used in technical laboratories. We shall not, perhaps, be wide of the mark in stating that 500,000 to 600,000 pounds weight of filter-paper of all grades is used in this country yearly.

Such a quantity of paper is obviously worth manufacturing here, but the amount being to a certain extent limited, as compared with other classes of papers, naturally led to the elimination of some of the paper manufacturers who had taken the matter up. We think we are right in stating that only four English paper makers are producing filter paper to-day.

For high-grade filter-paper various considerations have to be taken into account. The chemical and physical characteristics must be, as far as possible, co-ordinated, so that, while fulfilling certain requirements, such as retention of precipitates, the paper does not fail in some other important requisite, such as texture. Manufacturers have on the whole, however, rapidly marked out for themselves the proper lines to pursue, with the result that excellent products are on the market at the present time, and it will be admitted that these will easily stand comparison with those of the well-known German makers, Messrs. Schleicher and Schull. The paper makers started out to make a paper equal to this firm's 595 quality; but they soon found that they could do considerably better, as the number referred to was certainly not free from imperfection, it had many pinholes, and did not, in consequence, retain barium sulphate or other fine precipitates. The mineral matter was high, and therefore it was not a difficult problem to produce a better paper.

The essential features required in a filter-paper have necessitated a thorough grouping of papers according to the degree of purity required in certain work, but these groups have again to be subdivided into classes according to their physical characteristics. To make our meaning clearer let us take, for example, a pulp that has been prepared ready for making into paper. This pulp can be beaten by methods well known to the paper maker so as to produce papers ranging from those of the highest degree of softness and flexibility to those that are quite hard and transparent. For most filtering purposes it is necessary to have such papers as possess the character of "softness," and the technical term used for this is "bulk."

Bulk may be defined as the relation of volume of paper to volume of fibre, and, speaking generally, for a moderately rapid filter-paper the bulk should be about 3·5; fibre=1. From many determinations that we have carried out we have found them ranging from 3 to 4·5, the speed of filtration increasing as the bulk goes up. It is on this factor alone that we can judge into which sub-group a filter-paper should be put, and though the experience of a paper maker enables him to make a fair guess by the "handle" and weight of the paper, yet such a system does not

lend itself to any degree of accuracy, and is certainly not good enough for such a highly technical product. Regularity has doubtless been the reason of the popularity of the German makes, and it is essential that we in this country should follow on these lines.

Obviously the factor of bulk has its practical limits, not only from a manufacturing point of view, but also from its practical utility to the user. Taking papers bulking at 4.5, we have never found these free from pinholes, and we very much doubt if such could be made free from pinholes. In any case, we have never seen good sheets from a paper-making point of view, and more often than not they have been very bad. Such a class of paper, however, has its uses for manufacturing purposes in filtering varnishes, syrups, etc., because the particles in suspension are usually of a size that the paper is capable of retaining them, and even if at the start a certain amount passes through, a filtering medium of the particles themselves is quickly formed, and aids the clarification of the liquids.

For papers of high bulk used for the purposes just mentioned, another physical character is required—namely, high elasticity. This is measured directly by the stretch which the fibres undergo before breaking. Many papers have to stand the strain of liquids being forced through either by direct or diminished pressure, so that if a paper be weak fracture results.

Pinholes sometimes occur in papers of medium bulk—*e.g.*, about 3.5. This is due to faulty manipulation of the beaten stuff at the mill. Papers, however, showing this imperfection to a slight degree only, are frequently found in practice to be quite satisfactory in retaining many fine precipitates. This is partly due to the slight swelling of the ultimate fibre under the action of water, there is a gradual closing up of the sheet, but we believe it is mainly due to the air in the sheet being replaced by water, and the tension on the surface actually prevents the complete penetration of the particles through the paper.

We may illustrate by another example the importance of bulk in filter-paper in the use of the latter to differentiate between various dye stuffs by capillary attraction. When dye stuffs dissolved in water or other suitable solvent are dropped on paper, owing to their different colloidal characters, there is probably a rapid absorption and transmission over the surface, and an actual filtering out of the various colours. Obviously the greater the bulk the quicker will the colours be filtered out.

That there is a relation between the rates of absorption and of filtration denoted by this physical factor, bulk, is seen in the figures given on p. 162.

If a curve were plotted, using bulks as ordinates and rates of filtration as abscissæ, there would be almost a complete curve, with the exception of 3 and 4, which would be a straight line. This is possibly accounted for by an experimental error in calculating the bulk, as the thickness is taken as the mean between the reading obtained when the paper is squeezed fairly tightly and when the indicating dial is resting gently on the surface. We may mention that 3 and 4 were the same class of paper, only No. 4 had been subjected to a certain mechanical treatment to increase its apparent thickness, and therefore in this case bulk, to the extent of about 6 per cent.

Bulk. Fibre=1.	Rate of Filtration in Seconds of 100 c.c. Water at 20° C. through a 9-cm. Circle under a Constant Head.	Height in Cms. above Level of Liquid at 7·5° C.	
		After Five Minutes.	After Ten Minutes.
1. 3·06	360·0	2·1	3·0
2. 3·46	292·0	3·1	4·2
3. 3·59	160·0	3·4	4·7
4. 3·70	160·0	3·1	4·2
5. 3·89	115·0	5·4	7·4
6. 4·25	85·0	4·5	6·2
7. 4·28	69·8	4·8	6·5

So far we have dealt with the important question of physical qualities of filter-paper, and we now come to the chemical side of the matter.

In the manufacture of high-grade papers the cellulose obtained from flax or cotton is mostly used, and since paper is simply a compressed mass of fibre formed by the felting together of the ultimate fibre or its parts, the paper maker is able to utilise the waste material of the textile manufacturer either as yarn, fabric, or rags. In this particular class of paper cotton cellulose is preferable owing to its low hydrating power as compared with linen cellulose, under the action of beating, resulting in what is known as a "free" pulp. Such free pulp imparts the character of bulk to a paper. With this we have already dealt. It is difficult for the paper maker to get absolutely new waste material for making up into paper, and even if this were used the paper might not possess certain desired characteristics.

In a paper-mill the main questions in the production of various classes of paper are time and power. They are certainly the most important in filter-paper, as quickness in beating is an all-important feature. To obtain this one of the devices of the paper maker is to employ very sharp "tackle," and another is to use as far as possible old material. It is in the suitable selection of such material that chemists are more directly concerned, for the reason that many of the chemical impurities in the finished paper are usually directly traceable to this source. These impurities may be divided into inorganic and organic impurities.

Inorganic Impurities.—There is one impurity in filter-paper, namely, lime, which may be due directly to the water used in the manufacture. In most districts lime salts represent the chief constituent in the mineral solids of a water, and as the web of wet pulp after pressing still contains about twice the weight of water to weight of dry pulp, when the paper is dried, such lime salts are retained. The chemical operations in the mill during the purification of the material, such as bleaching, also contribute towards this impurity. It is easy therefore to appreciate the difficulty the paper maker is confronted with. Even when softened water is used it is frequently only a case of replacing one impurity to a certain extent by another.

In addition to lime, the chief impurity is iron oxide. It is very rare that metallic iron is present as such in the paper, but if it be so, as a rule it can be

traced to the presence of fragments of iron hooks, buttons, etc., which get carried through between the roll and bedplate of the beater. Only careful sorting, or other devices for removing iron, such as would be used in making ashless papers, can be resorted to by the paper maker. Copper is another impurity that is frequently found.

The atmosphere and dirt contain a considerable amount of iron, and, therefore, rags that would be used in paper-making would not be chemically pure. It is quite conceivable that, owing to the phenolic hydroxyls in the cellulose complex, there is to a certain extent an affinity between the basic iron and the cellulose itself. Only a treatment with a more powerful electro-negative radicle could be expected to break this bond, and, of course, such a treatment is applied in the making of ashless papers.

Sometimes silica and alumina are found, and this is, doubtless, due to the loading of fragments of rags with kaolin.

Organic Impurities.—These consist practically of only two—namely, starch and oil.

Starch is generally present in old rag material as a dressing, but it is largely dissolved or swollen up in the alkaline boil to which the rags are subjected, and finally removed in the subsequent washing. Some paper-makers use other methods to effect a complete removal. The absence of starch is desirable, as under the treatment of alkali it passes more or less into a soluble form, and this, if left in the paper, has a certain sizing effect.

Oil.—Traces of oil are generally found in filter-paper, but the amount is usually very small. In samples examined recently only 0.07 to 0.084 per cent. has been found. Sometimes the raw material contains as much as 1.0 per cent. of fatty matter, but this is saponified under the caustic alkali treatment, and is ultimately washed away.

The estimation of fat in milk by the Adams method can be done on strips of paper of the usual size. We should, however, advise a trial test to be carried out on one coil in order to estimate the amount of matter soluble in ether. The correction can then be used for the whole batch of paper bought, for such a strip would be one of a large making of paper. Doubtless in time English paper makers will supply fat-extracted papers.

In special cases, of course, the chemist can, if he so desire, extract about thirty circles at a time for about thirty minutes with ether. It would, therefore, be little trouble to keep one box of filter-paper fat-free.

DISCUSSION.

Mr. W. T. BURGESS remarked that if, for instance, a dozen circles from a packet of any brand of filter-paper were weighed, the probability was that one would weigh 20 or 25 per cent. more than another—*i.e.*, there was a possible error of ± 10 or $\pm 12\frac{1}{2}$ per cent. on the average. This applied not only to English, but also to standard German papers; indeed, the former appeared to compare favourably in this respect with the latter. It seemed to him, without knowing the actual weights of the papers used for the authors' experiments, that an average error of ± 10 per cent.

might be sufficient to throw some of the figures out of order in the tables shown by the authors.

Mr. A. W. KNAPP said that there were great possibilities for experiment in the direction of producing paper suitable for the Adams process—*i.e.*, paper which yielded no ether-soluble matter and no fluff.

Mr. E. HINKS said that the rate of filtration depended a great deal on the funnel, the difficulty being to get funnels sufficiently alike to render the results comparable as regards the paper.

Mr. L. ARCHBUTT was surprised to hear that such a pure article as filter-paper was made from old rags; he should have thought it would have been necessary to go farther back and start with a purified raw material. One could understand the difficulty of making ashless or even approximately ashless papers by the ordinary methods, unless the manufacture were carried on at a place like Lancaster or Morecambe, which had exceptionally pure natural water; but would it not be practicable to use distilled water for the final wash? If that were done, the nature of the other water would seem not to be of much moment.

Mr. E. M. HAWKINS said that, while the Adams papers usually yielded an appreciable quantity of extract to ordinary ether, he had found that comparatively little was extracted when petroleum spirit or carbon bisulphide was used.

Dr. DYER recalled the fact that Dr. Vieth had pointed out many years ago, when the Adams process was new, that paper contained not only matters extractable by ether, but also saponified resinous matters, and that milk in drying was apt to become acidified, and thus to liberate resin soluble in ether. The paper, therefore, should be prepared beforehand by acidifying, washing, drying, and extraction with ether. In this way accurate results were obtainable.

Mr. E. R. BOLTON said that for filtering fats, syrups, etc., rapidly and thoroughly in the laboratory, he had been accustomed to use Schleicher and Schull's No. 604 papers, which gave such good results that he had not expected them to be equalled by English paper. On trying a No. 4 English paper, however, beside one of Schleicher and Schull's, he had found that there was really very little to choose between them. The English paper filtered somewhat more slowly, but much more perfectly in one filtration, than the other.

Mr. C. H. CRIBB remarked that in Mr. Bacon's table the paper showing the highest "bulk" had not the greatest absorptive power. He should have thought that the surface tension of water would have been sufficient to bridge over any pinholes, etc., that would be likely to occur in any filter-paper that was of practical use.

Mr. BACON, in reply, said that papers were certainly liable to differ in weight, as Mr. Burgess had mentioned, and, indeed, this was not surprising considering the nature of the process of manufacture. The series of papers taken for these experiments were practically all of the same weight and substance, but a moderate difference in weight would make very little difference in the degree of absorbency and rate of filtration, since what was measured was merely the relationship of volume of fibre to volume of air. A large increase in weight, however, did seem to make some difference, for which he could not account, except that perhaps there was a limit at which the effect of the increased amount of fibre diminished the air space, and

so reduced the rate of filtration. The presence of resinous matter in the paper was easily accounted for by the natural presence of resin in the cotton fibre. He agreed with Mr. Hinks's remark as to funnels. In their experiments they had tried as far as possible to insure that the funnels used were of uniform shape, and they were careful always to fold the filter-paper in such a way that it lay close to the funnel. This latter point was important; if the paper were not in close contact with the funnel all over (except for the cone just at the bottom), the rate of filtration would be enormously increased. The materials used were both old rags and purified raw material, and it was upon the careful blending of these two that success in the manufacture depended. Purified raw material by itself would not yield all the characters that were needed in high-class filter-paper. In the old material a certain amount of oxycellulose, resulting from oxidation, was produced, which could not to be regarded quite as an impurity. In some special cases distilled water was used for the final wash. He could not account for the difference in absorptive power between samples No. 5 and No. 6. An analysis of these two samples showed that No. 6 contained a considerable proportion of fatty matter, whereas No. 5 had practically none.



THE ESTIMATION OF POTASSIUM IN PRESENCE OF OTHER SUBSTANCES.

By ALEX. H. BENNETT.

(Read at the Meeting, April 5, 1916.)

In two recent papers (W. A. Davis, *J. Agric. Science*, 1912, **5**, 52 and Thin and Cumming, *J. Chem. Soc.*, 1915, **107**, 361) attention has been drawn to the advantages of the perchlorate method for the estimation of potassium, and it has been shown that, with the precautions described, accurate quantitative results are obtained in the presence of considerable quantities of other chlorides (up to 2 grms.—Thin and Cumming), while Davis has shown that potassium in the form of sulphate can be satisfactorily estimated without previous precipitation with barium chloride. The presence of other sulphates, however, interferes with the results, and the method cannot, of course, be directly applied to solutions containing organic matter. I have also found difficulties in cases—for example, in the mother liquors of salt works—in which it is desired to estimate small quantities of potassium in the presence of very large amounts of sodium and magnesium salts. In such cases either the total amount of salts present in the analysis must be too great to be conveniently handled or the amount of potassium will be too small for accurate estimation.

There have been many attempts to make use of the highly insoluble potassium cobaltinitrite for the purposes of quantitative estimation, but apparently no very high degree of accuracy can be claimed for the results. The precipitate is not constant in composition. According to Mitscherlich and Fischer (*Analyst*, 1912,

37, 588), with increasing proportions of the reagent the amount of sodium entering the molecule of the product increases at the expense of the potassium, and the composition of the precipitate approaches a limiting value after a certain excess has been added—that is, more than thirty parts of sodium to one of potassium.

If, however, the potassium cobaltinitrite precipitate is redissolved by heating with dilute hydrochloric acid and the solution evaporated with perchloric acid following the usual procedure, the potassium perchlorate is obtained in the pure state, the perchlorates of sodium and cobalt being readily soluble in alcohol, and the estimation of the potassium can thus be accurately carried out.

The cobalt reagent is prepared as follows: Fifty grms. of cobalt nitrate and 300 grms. of sodium nitrite are dissolved in water, acidified with 25 c.c. of glacial acetic acid and diluted to a litre. After standing twenty-four hours the solution is filtered and is ready for use.

The delicacy of the test depends largely on the concentration of the reagent in the liquid under examination, as is shown in the following experiments:

Three portions of a solution containing in each portion 5 mgrms. of potassium chloride in 100 c.c. of water were treated with 15, 30, and 50 c.c. of the cobalt reagent respectively.

- With 15 c.c.: No precipitate after several hours.
- „ 30 c.c.: Faint turbidity after an hour.
- „ 50 c.c.: Precipitate after ten minutes.

Fifty c.c. of a solution containing 2 mgrms. of potassium chloride gave with 15 c.c. of the reagent no precipitate after several hours, but with 30 c.c. gave a precipitate in the course of half an hour.

For an estimation, therefore, the cobalt reagent is added to the proportion of 30 c.c. to every 50 c.c. of the solution containing potassium (the amount of the latter may be conveniently from 0.1 to 0.2 gm.). After standing for a couple of hours the precipitate is filtered off, using the filter pump, and washed with water containing a small amount of the cobalt solution. If pure water be used there is some tendency for the precipitate to pass through the filter. It is convenient to use a perforated porcelain plate covered with a disc of filter-paper. After washing, the precipitate and filter are returned to the beaker, and the precipitate dissolved in a small volume of hot dilute hydrochloric acid and the solution filtered into a small porcelain or silica evaporating basin. The total volume of filtrate and washings is easily kept down to between 60 and 80 c.c. The liquid is then evaporated to dryness on the water-bath and the residue redissolved in hot water (should there be any insoluble matter, it can be removed by filtration at this point), and the solution treated with 3 to 6 c.c. of perchloric acid, according to the amount of potash present, and again evaporated to dryness. It is well to wash down the residue with a few c.c. of hot water and again evaporate, in order to make sure that the conversion into perchlorates is complete.

When cool, 25 c.c. of 98 per cent. alcohol are added, the mixture stirred well, and after a short time filtered through a Gooch crucible, washed with alcohol which has been acidified with 2 per cent. of perchloric acid and saturated with

ESTIMATION OF POTASSIUM IN PRESENCE OF OTHER SUBSTANCES 167

potassium perchlorate as described by the authors already quoted, then dried at 100° C., and the potassium perchlorate weighed.

The solution for precipitation with the cobaltinitrate reagent may be neutral or acid up to about normal strength. If too strongly acid the nitrites will, of course, be decomposed, and to avoid this the solution must be partly neutralised with soda. In this connection I have found that "pure" sodium hydroxide is apt to contain appreciable traces of potash. The carbonate is better in this respect.

Some of the results obtained under varying conditions are shown in the following table:

Taken.	Found.
0.2000 grm. KCl in 50 c.c. water	0.2008 grm.
0.2000 " K ₂ SO ₄ " " "	0.2006 "
0.2000 " " " " and 1 c.c. strong H ₂ SO ₄	0.2005 "
0.2000 " " " " of a saturated solution of NaCl	0.1994 "
0.2000 " " in 50 c.c. of a solution containing 25 grms. MgCl ₂ and 1 c.c. HCl	0.2000 "
0.2000 " " in 50 c.c. water with 1 grm. FeCl ₃	0.1990 "
0.2000 " KCl in 50 c.c. water with 1 grm. Na ₂ HPO ₄	0.1998 "
0.2000 " " in 100 c.c. water	0.1991 "
0.2000 " " in 50 c.c. water containing 12 grms. sugar	0.2000 "
0.2000 " " in 50 c.c. of 5 per cent. citric acid solution	0.2004 "
0.2000 " " in the same solution neutralised with Na ₂ CO ₃	0.2006 "

The method can be usefully applied to the estimation of potassium in wine lees, argols, and tartars, and in the liquors of tartaric acid works where it occurs in presence of free tartaric and sulphuric acids, phosphoric acid, iron and alumina and organic matter. As examples of this:

- 0.5 grm. of pure potassium bitartrate dissolved in 5 c.c. of hydrochloric acid (of 1.10 sp. gr.) and diluted to 50 c.c. Found 0.5005 grm.
- 0.25 grm. bitartrate dissolved with 2 c.c. concentrated H₂SO₄ and 5 grms. tartaric acid, the whole neutralised with Na₂CO₃. Found 0.2499.

Potash was estimated in a sample of argol, using the dilute hydrochloric acid extract of the sample, and 19.04 per cent. K₂O was found. The same sample after incineration contained 18.94 per cent. K₂O. In a sample of wine lees, 11.54 per cent., and 11.44 per cent. of K₂O was found.

When the acid solution to be examined contains phosphates of iron and aluminium in any quantity, these will be precipitated with the cobaltinitrite and will interfere with the results. This can be avoided by the addition of sufficient sodium citrate to keep the phosphates in solution when the cobaltinitrite reagent is added. The results in this case are quite accurate, as is shown in the following examples:

1. A mixture containing 0.2000 grm. KCl with 0.5 grm. sodium phosphate, and an equivalent amount of ferric chloride and sufficient acid for solution was made,

and a solution containing 3 grms. citric acid neutralised with soda was added. Found 0.2008 gm.

2. A similar mixture containing 0.1000 gm. KCl. Found 0.1003 gm.

This method can be successfully applied to the direct estimation of potassium in solution in the presence of even large quantities of other substances, ammonium salts being the only ones of common occurrence which are capable of interfering with the results.

DISCUSSION.

Dr. J. A. VOELCKER said that Dr. Leather, the Agricultural Chemist to the Government of India, had recently done a good deal of work in comparing the perchlorate method with the platinum method, and had found the perchlorate method to work perfectly well when the quantity of potash was fairly large, but that with small quantities, such as were dealt with by the present author and such as were met with in the case of soils, it did not give such satisfactory results as the platinum method.

Mr. E. R. BOLTON said that he had used the perchlorate method for the estimation of what might be called considerable quantities of potash, but had no reason for thinking that it would be unsuitable when the quantity was small; but he quite anticipated that there might be difficulties owing to the presence of substances referred to by the author. If there were any difficulty under such circumstances, the cobaltinitrite method would seem likely to be of great assistance for the preliminary separation, though he had not himself had any experience of its use. With regard to the composition of the potassium cobaltinitrite precipitate, the quantity of sodium taken up would only affect the weight of the precipitate, which did not matter, since the author's results indicated that the potassium was entirely precipitated.

Mr. E. M. HAWKINS remarked that one of the advantages of the cobaltinitrite process was that it was not interfered with by sulphates. Like the author, he had noticed that ordinary caustic soda frequently contained such quantities of potash as to make its use inadmissible for this purpose without special precautions.

Dr. DYER said that he had used the perchlorate method a good deal, and had found it satisfactory, even for small quantities of potash.



NOTE ON A SPECIMEN OF ANCIENT RUSSIAN OAK.

By P. A. ELLIS RICHARDS, F.I.C.

(Read at the Meeting, April 5, 1916.)

THE particular wood that forms the subject of this note has been recently introduced into this country with the intention of using it for the same purposes as ordinary oak. It is obtained in fairly large quantities from the province of Krasnoslobodsk in the Government of Penza, Central Russia. The trees from which the oak is obtained are found more or less covered by soil in the old bed of the River Moksha, which flows along a valley from five to seven miles in width enclosed by mountain ridges of moderate height.

It would appear that in bygone days the river was much broader and deeper than it is now, and at various periods in its history has changed its course, flowing at one time over tracts of forests and at a later time leaving the buried trees more or less uncovered except for the sand that has silted over them.

The age of the wood now recovered is estimated to be at least 1,000 years, yet so well has it been protected from disintegration that it still retains its woody texture although its colour has changed to a grey or dull brown tint.

It is interesting to note the effect on the mineral constituents present when the wood has been exposed for so long a period to contact with moist sandy soil.

The total ash obtained from a specimen of the oak was 1.12 per cent., and only 14.2 per cent. of the total mineral matter was soluble in water. Another piece of oak, darker in colour than the former, gave a total ash of 2.21 per cent., and of this only 23 per cent., consisting entirely of calcium sulphate and oxide, was soluble in water. The colour of the ash in each case was deep reddish-brown, somewhat resembling cocoa in tint. Two samples of ordinary oak were examined at the same time for comparison purposes, and they yielded 0.49 per cent. and 0.32 per cent. of ash respectively. In these cases the ash was greyish-white, and the percentages soluble in water were, in the one sample 49.6, and in the other 53.4.

The specific gravities of the two Russian oaks were 0.73 and 0.79, and of the two pieces of English wood 0.65 and 0.69.

The following figures give the composition of the specimens examined:

COMPOSITION OF WOOD.

	Russian Oak.		English Oak.
	No. 1 (<i>Grey</i>).	No. 2 (<i>Black</i>).	No. 3.
Mineral matter	1.12	2.21	0.49
Ether + alcohol extract	3.26	2.51	8.23
Water and total extractives	39.7	47.4	39.9
Cellulose	33.6	31.0	34.6
Lignin, etc.	26.7	21.6	25.5

COMPOSITION OF MINERAL MATTER.

	Russian Oak.		English Oak.	
	No. 1 (<i>Grey</i>).	No. 2 (<i>Black</i>).	No. 3.	No. 4.
Fe ₂ O ₃	49.73	69.45	1.28	2.01
Al ₂ O ₃	0.86	1.98	6.48	4.87
CaO	22.53	24.12	22.79	9.3
MgO	0.49	Nil	3.12	9.1
SiO ₂	7.56	Trace	2.52	3.64
SO ₃	4.49	2.02	Nil	Nil
CO ₂ combined with Ca and Mg	12.24	2.43	18.2	17.32
Na and K salts	2.1	Trace	45.61	53.76

When the figures so obtained are calculated in terms of the original wood, it is found that the amount of ferric oxide is practically the same in both specimens of English oak, and that the proportion in Russian oak No. 2 is 240 times as much. The calcium oxide content in the latter is in the one case four times and in the other nine times as much as the sum of the oxides of calcium and magnesium in the two English samples.

It would seem that the prolonged solvent action of the river water in the presence of a sandy soil rich in iron has resulted in a large increase in the iron and silica content, and in the substitution of calcium compounds for the salts of sodium and potassium originally present, the wood still retaining to a great extent its natural characteristics.

DISCUSSION.

Mr. W. J. A. BUTTERFIELD asked if any information was available on such points as the presence of sphagnum or other peaty matter in the water or in the wood, the presence of any considerable proportion of iron in the water, and the temperature conditions; and also whether the wood occurred in large or in small pieces.

Dr. J. A. VOELCKER remarked that the most striking feature in this case seemed to be the substitution of iron salts for alkalis. It would be interesting if some more information could be given regarding the two samples of English oak. These differed a good deal—for instance, in regard to their lime contents—and one would naturally ask whether such differences were due to differences of soil or to other natural conditions. If they were, it was not surprising to find even much larger differences occurring in such cases as the author had brought forward.

Mr. J. H. B. JENKINS asked how this wood which had been submerged compared with wood grown in the same district, but which had not been submerged. The substitution of iron for alkali, as seen in the ash, reminded one of the way in which, in fossils, the calcium carbonate originally present was sometimes replaced by pyrites.

Dr. J. T. DUNN said that when some years ago the foundations of the old Tyne bridge at Newcastle were dug up for the purpose of erecting the present swing-bridge, a considerable quantity of oaken piles were found, which were supposed to date from Roman times; at any rate, they must have been there for many hundreds of years. The oak was taken out of the bed of the river in a perfect state of preservation, and much of it was used for making furniture. In that case, of course, the river was a tidal one.

The PRESIDENT said that there was a forest bed under the river Severn, near Sharpness, and specimens of wood dug from it, which were possibly many thousands of years old, were all well preserved, like those shown by Mr. Richards. As to the effect of oxide of iron, he had known of cases in which lakes choked with all kinds of vegetation had been rendered perfectly clear when particles of red sandstone had been allowed to wash into them. A large part of Russia was covered by Permian sandstone, and possibly the water had passed through that.

Mr. RICHARDS said that the Moksha River was somewhat like the Mississippi, in that it had changed its course occasionally. The forest, which stretched for hundreds of miles, at the present day skirted the banks, but the old bed of the river lay some miles away. From time to time the river flowed through the forest, sweeping away the trees, which became covered with ferruginous and sandy soil. He could not say whether the water contained iron, but probably it did, as there was a good deal in the sand. The wood was found in large logs—in fact, as whole tree-trunks. It was true that the two specimens of English oak differed somewhat in mineral constituents, but the ash of the Russian oak was of an entirely different character.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Composition of Roman Pomade. L. Reutter. (*Comptes rend.*, 1916, **162**, 470-471.)—A Roman vase discovered at Ticino contained a yellow ointment, which melted at about 58° C., and was partially soluble in petroleum spirit and ether. The analysis indicated that it consisted of a mixture of beeswax and fat, with the addition of storax and oil of turpentine. The presence of tartrates suggested that it had been macerated with wine, while the colour was apparently due to henna.

C. A. M.

Researches on the Detergent Action of Soap. S. A. Shorter. (*J. Soc. Dyers and Col.*, 1916, **32**, 99-109; through *J. Soc. Chem. Ind.*, 1916, **35**, 549.)—The observations in connection with these researches were carried out with the stalagmometer,

an instrument of the type of a pipette, filled with benzene or other immiscible liquid, designed to deliver drops from its upturned point when held below the surface of the solution to be tested. The number of drops formed in the discharge of a measured volume was counted, giving the "drop number," which is approximately inversely proportional to the surface tension; a large drop number corresponds to a large "surface activity." In a solution of soap consisting of free alkali and acid soap resulting from hydrolysis, the latter exercises no "surface activity"; this was proved by means of the stalagmometer filled with pure benzene when immersed in soap solutions to which increasing quantities of hydrochloric acid were added. As the decomposition of the soap progressed, the drop number fell until it became practically equal to that obtained with pure water. The influence of alkali in soap solutions was studied by adding oleic acid to the benzene and comparing the increased drop number with that of pure benzene; soap solutions containing various ratios of alkali to fatty acid were employed. In a "neutral" soap solution, with molecular ratio of acid: alkali = 1.0, the "surface activity" of the free alkali due to hydrolysis was only about one-fifth of that of the undecomposed potassium oleate; it was slightly more in a more alkaline soap, and considerably less in one with higher acid: alkali ratio. The "surface activity ratio" increased only slightly with increase in concentration of the soap solution, because the degree of hydrolysis decreases in more concentrated solutions. Hence the detergent action of solutions of neutral or slightly alkaline soaps is due mainly to the undecomposed soap. The view that the detergent action of soap is due to its colloidal nature is supported by observations carried out on "Sapon," an alkaline detergent containing no fat, prepared by the action of strong alkalis on cereals. This colloid detergent showed a "surface activity" in the stalagmometer comparable with that of soap solutions; this method, therefore, is capable of determining the value of a detergent containing "surface active" colloids other than salts of fatty acids. The addition of alkali to a soap solution increases the "surface activity" of the soap, even to pure benzene, and its detergent action is improved, probably by a modification in a favourable sense of its colloidal condition; the addition of saline electrolytes also increases the "surface activity," but in a minor degree. It is suggested that this action of alkali on the soap may be quite as important as its specific action on the fatty acids of the grease.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Peroxydase Reaction in Milk. W. Grimmer. (*Milchw. Zentr.*, 1915, **44**, 246-247.)—Guaiacol and ethyl hydroperoxide possess distinct advantages over guaiacum tincture and hydrogen peroxide as reagents for the detection of peroxydase in milk, since their solutions are stable for a period of several years. The test is carried out by mixing a few c.c. of milk with 2 drops of guaiacol solution (1 gm. of guaiacol dissolved in 10 c.c. of alcohol and diluted with water to 100 c.c.), and then adding 2 drops of a 0.1 per cent. ethyl hydroperoxide solution. A brick-red coloration is obtained with unheated milk, whilst boiled milk remains colourless.

W. P. S.

Estimation of Albumin in Urine. R. Dhommée. (*J. Pharm. Chim.*, 1916, 13, 241-249.)—A mixture of trichloroacetic acid and picric acid precipitates albumin from urine within ten minutes in the cold. The reagent may be made in either of the following ways: (1) Picric acid, 10 grms.; trichloroacetic acid, 10 grms.; glacial acetic acid, 100 grms.; and water, to 1 litre. (2) Picric acid, 5 grms.; trichloroacetic acid, 10 grms.; citric acid, 25 grms.; and water, to 1 litre. Either reagent is capable of detecting 1 part of albumin in 50,000 parts of urine. For quantitative estimations 10 c.c. of the filtered urine are shaken for a few seconds with 5 c.c. of reagent (2) in a centrifugal tube the tapering end of which is graduated in tenths of a c.c., and allowed to stand for ten minutes. The tube is then centrifuged for three minutes at a speed of about 1,800 revolutions per minute, the volume of the deposited albumin read, and the weight found by reference to the following table:

Weight of albumin per litre, grms.	0.0625	0.125	0.25	0.50	1	1.5	2	3	4	5	6	7	8
Volume of precipitate, c.c.	Precipitate not measurable	0.12	0.2	0.4	0.7	1.0	1.4	1.9	2.15	2.4	2.7	2.9	3.0

In the case of urines containing more than 3 grms. of albumin per litre dilution is necessary.

C. A. M.

New Reaction of Urine. A. Bach. (*Comptes rend.*, 1916, 162, 353-354.)—The reduction of nitrates and colouring matters in animal tissues has been proved to be the result of the action of an enzyme and a co-enzyme, neither of which separately has any reducing effect. Fresh milk contains the enzyme unaccompanied by the co-enzyme, and only reduces nitrates when substances containing the co-enzyme or its equivalent (*e.g.*, aldehydes) are added. Commercial peptones and albumin completely degraded to amino acids furnish the necessary aldehydic bodies to function as a co-enzyme. It is now found that urine, in virtue of the presence of the products of degradation of proteins, may serve in conjunction with the enzyme present in fresh milk to bring about the reduction of nitrates, and the nitrate formed is readily estimated by colorimetric tests. Three c.c. of fresh urine are mixed with 2 c.c. of milk and 0.2 gm. of pure sodium nitrate, and digested for twenty minutes at 60° C. At the same time a blank experiment is run with milk and urine without the nitrate. At the end of the digestion, 5 c.c. of Illosvay's reagent (a mixture of sulphanilic acid and α -naphthylamine in dilute acetic acid) are added to each, and the red coloration developed by the nitrite in the one is matched by the addition of a standard solution of nitrite to the blank test. For a more exact estimation, 15 c.c. of urine and 10 c.c. of milk are taken for each test, and 1 gm. of sodium nitrate is added to the one. After digestion both mixtures are clarified by the addition of 0.5 gm. of finely powdered basic lead acetate to each, and filtered through dry papers; the nitrite is estimated colorimetrically in 20 c.c. of filtrate. A number of experiments showed that 1 c.c. of normal urine, in conjunction with the enzyme of milk, is capable of reducing nitrate equivalent to 0.00001-0.00005 gm. of N_2O_5 . Blood-serum collected under aseptic conditions does not reduce nitrates in presence of milk, but after modification by bacteria the serum gives a strong reaction.

J. F. B.

ORGANIC ANALYSIS.

Analysis of Commercial Benzols. P. E. Spielmann and E. G. Wheeler. (*J. Soc. Chem. Ind.*, 1916, 35, 396-399.)—The following method is described for estimating the percentages of benzene, toluene, paraffin, and carbon bisulphide, in a properly washed commercial benzol :

Estimation of Toluene.—One hundred c.c. of the sample are distilled from an Engler flask at the rate of 7 c.c. per minute, proper precautions being taken with

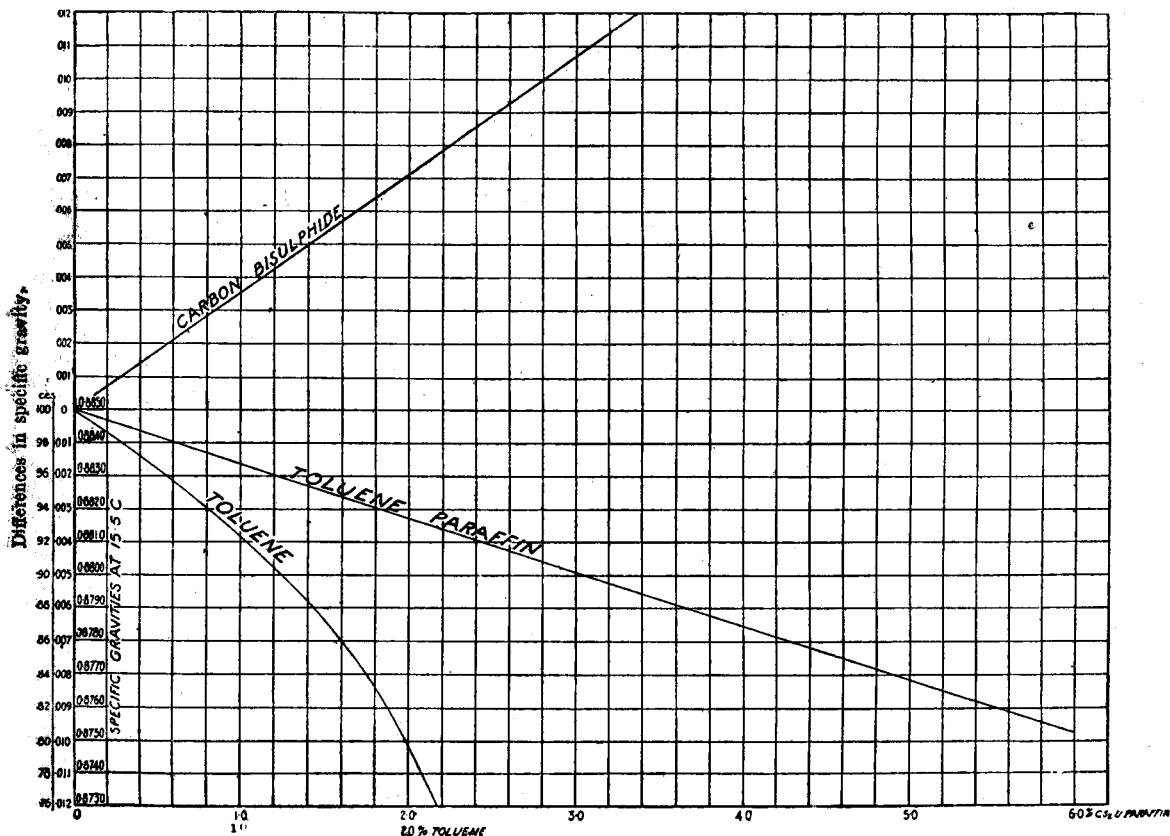


FIG. 1.

regard to draughts and the efficient condensation of the distillate ; the volume in c.c. passing over up to 90° C. indicates the quantity of toluene present when reference is made to a previously constructed curve. Paraffin and carbon bisulphide, in the quantities occurring normally in commercial benzols, do not interfere. The method is reliable up to a toluene content of 20 per cent. ; above this quantity the methods described by Colman (*ANALYST*, 1915, 40, 166, 170) and Northall-Laurie (*ibid.*, 1915, 40, 384) are the more accurate.

Estimation of Carbon Bisulphide.—The benzol is treated with alcoholic potassium hydroxide solution, washed to remove the xanthate, alcohol, etc., and dried ; its sp. gr.

is then determined. The difference between the sp. gr. of the original sample and the sp. gr. thus obtained is proportional to the quantity of carbon bisulphide present, and can be found by reference to a curve (see Fig. 1).

Estimation of Paraffin.—After removal of the carbon bisulphide, the mixture consists essentially of benzene, toluene, and paraffin. The quantity of toluene has

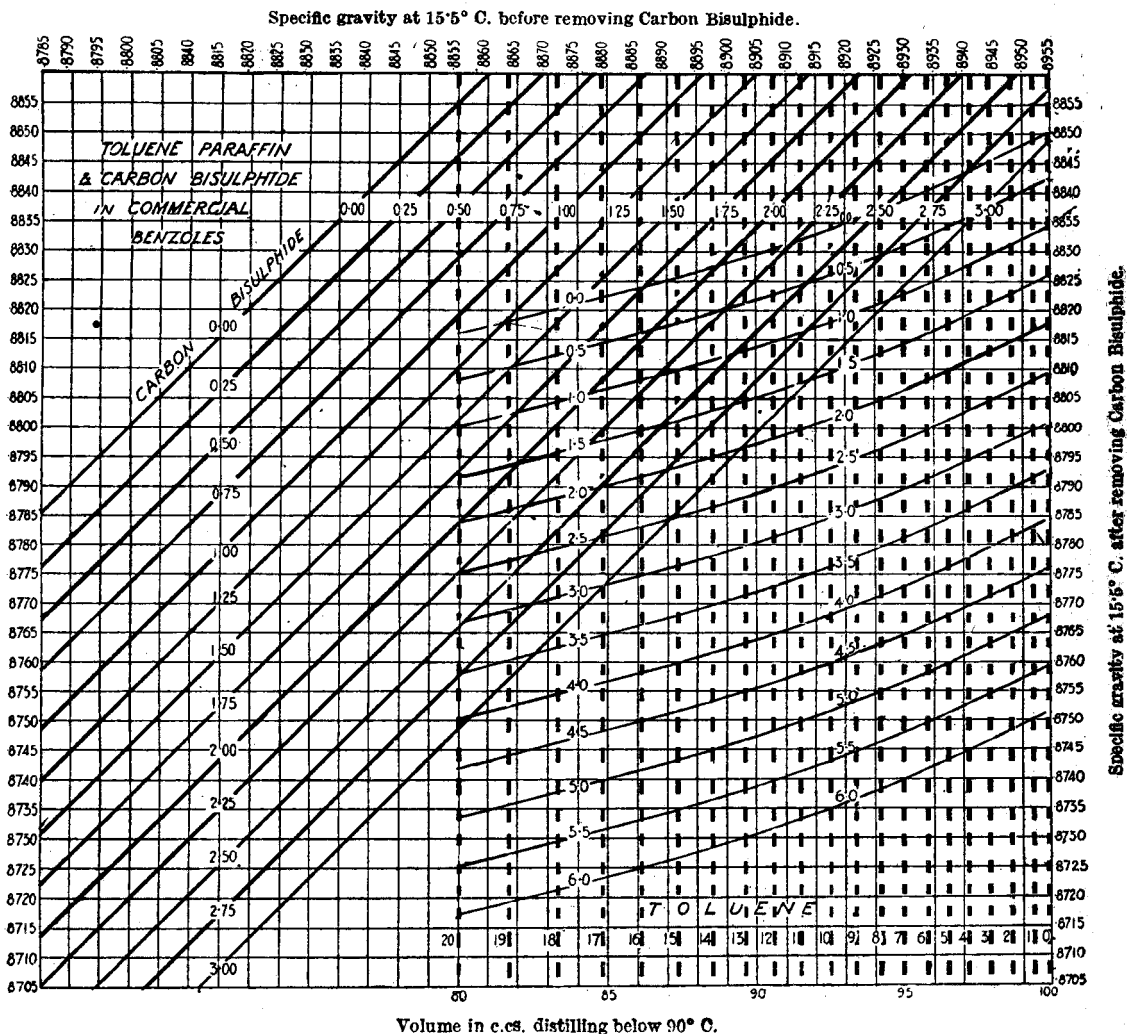


FIG. 2.

already been found, and the sp. gr. of a mixture of benzene and this quantity of toluene can be found from a previously constructed curve, so that the difference between the sp. gr. of the benzene-toluene mixture and that of the sample after removal of the carbon bisulphide is proportional to the quantity of paraffin present, the actual value of which is found from the curve given.

Estimation of Benzene.—This constituent is taken by difference.

Some benzols contain thiophene, but this is rarely present to the extent of more than 0.5 per cent., a quantity which would cause an error of 0.3 per cent. in the amount of paraffin found; as this is within the limits of accuracy of the method, it can be neglected. The average limit of accuracy of the method is—toluene, 1 per cent.; paraffin, 0.5 per cent.; carbon bisulphide, 0.1 per cent.

In Fig. 1 are collected the curves showing the effects on the sp. gr. of benzene, toluene, carbon bisulphide, and paraffin, together with the toluene distillation curve. For the sake of convenience in working, the curves shown in Fig. 2 have been constructed. Here it is not even necessary to determine the various differences in sp. gr.; only the observed figures need be dealt with. The analytical results are interpreted as follows: The number of c.c. distilling below 90° C. represents the percentage of toluene. This number of c.c. has been plotted against the sp. gr. found after removal of the carbon bisulphide in such a manner that the percentage of paraffin is read off directly. The sp. gr. of the sample has been plotted against the sp. gr. after removal of the carbon bisulphide, whereby the percentage quantity of the latter can be read off.

W. P. S.

Optical Dispersion of Chinese Wood Oil as an Index of Purity. E. E.

Ware. (*J. Ind. and Eng. Chem.*, 1916, 8, 126-128.)—The method of examination used by Brier (*ANALYST*, 1916, 13) may be simplified by making a direct reading of the dispersion of the oil, which for this purpose is placed in a hollow prism in a spectrometer, with a brass electrode arc lamp as the light. An estimation is made of the relative dispersion for two lines given by this light in the red and the blue part of the spectrum. The angular difference for Chinese wood oil contained in a prism with an angle of 20° 1' was found to be 26' 54", while for soya bean oil at the same temperature it was 12' 54", or, expressed in vernier units of 6" each, the readings were 269 and 129 respectively. The dispersion of Chinese wood oil adulterated with varying proportions of soya bean oil may be expressed as a straight line, when percentage adulteration and angular dispersion are plotted respectively as co-ordinates. It is suggested that by fitting the spectrometer with a constant temperature device adulteration of Chinese wood oil could be rapidly detected by the variations in the angular readings. The correction for temperature is about one second per 1° C., which corresponds to about 0.1 per cent. of adulteration.

C. A. M.

Heat of Bromination of Fats and Oils. J. W. Marden. (*J. Ind. and Eng.*

Chem., 1916, 8, 121-126.)—The calorimeter used for measuring the heat of bromination consisted of a large Dewar vacuum-tube containing a special mixing chamber of copper, coated inside with paraffin wax, and fitted with a glass cover which rested on a flange about halfway up, so as to divide the chamber into two compartments. In the lower of these was placed the oil, while a solution of bromine in three times its weight of carbon tetrachloride was placed in the upper chamber. The liquids were brought into contact by breaking the cover-glass by means of a paddle-stirrer within the chamber, and mixture was effected by rotating the mixing chamber. A

smaller calorimeter, consisting of a Dewar tube (3 × 20 cm.) containing a thin glass tube (0.8 × 23 cm.), with copper wire stirrers in both tubes, was used for measuring the specific heat of brominated oils, and both calorimeters were standardised by determining therein the heat of dilution of standard sulphuric acid. The calories per grm. of oil were calculated by adding the heat capacity of the apparatus to that of the mixture of bromine solution and oil, multiplying by the total rise of temperature, and dividing the result by the grms. of oil used. The following table gives results thus obtained, together with the relationship of the values to the iodine values:

Oil or Fat.	Heat of Bromination.	Iodine Value found.	Iodine Value calculated. Factor, 0.846.	Deviation per Cent.
	Cals. per Grm.			
Sandalwood	274.0	270.0	232.0	-14.1
Raw linseed	206.0	172.5	174.2	0.98
Boiled linseed	204.6	169.0	173.0	2.36
Chinese wood	150.0	156.0	127.0	-18.6
Maize	146.2	123.1	123.8	0.57
Sesame	126.4	108.2	107.0	-1.12
Rapeseed	120.8	105.8	102.2	-3.4
Cottonseed	117.0	101.7	99.0	-2.6
Sperm	109.0	93.4	92.2	-1.28
Castor (purified)	104.1	88.8	88.1	-0.79
„ (commercial)	102.2	87.5	86.5	-1.14
Arachis	102.2	83.2	86.5	3.96
Olive, I.	100.7	84.0	85.2	1.43
„ II.	96.6	80.0	81.7	2.12
„ III.	95.4	80.3	80.7	0.5
Neat's foot	83.0	68.7	70.2	2.2
Lard	79.3	68.6	67.2	-2.04
Mineral	nil	—	—	—

The method cannot be used for testing oil of turpentine, owing to the solubility of the paraffin wax in that liquid. The cases where there was marked deviation between the calculated and determined iodine values was attributed to there being a greater amount of substitution of the bromine (see Hehner and Mitchell, *ANALYST*, 1895, 20, 148).
C. A. M.

Oils of the Coniferæ. V. The Leaf and Twig and Bark Oils of Incense Cedar. A. W. Schorger. (*J. Ind. and Eng. Chem.*, 1916, 8, 22-24.)—Incense cedar (*Libocedrus decurrens*) is largely restricted in its range to the State of California. The leaves and twigs, if stored for a few weeks, show a slight increase in the yield of oil as compared with the fresh material. The majority of leaf and twig oils were pale greenish-yellow in colour, a few being dark greenish-brown; their properties were: Specific gravity at 15° C., 0.8655 to 0.8766. Refractive index, at 15° C., 1.4754 to 1.4778. Optical rotation, $[\alpha]_D^{20^\circ C.}$, -3.2 to +38.7. Acid number, 0.48

to 1.3. Ester number, 18.5 to 27.82. Ester number after acetylation, 28.6 to 46.2. Acetate per cent., 6.47 to 9.74. Free alcohols per cent., 2.26 to 5.14. Total alcohols per cent., 8.28 to 12.8.

The bark oil had the following properties: Colour, faint greenish-yellow. Specific gravity at 15° C., 0.8621. Refractive index at 15° C., 1.4716. $[\alpha]_D^{20} + 1.1$. Acid number, 0.6. Ester number, 3.22. Ester number after acetylation, 9.53.

The following table shows the approximate percentage composition:

	Leaf and Twig Oil.	Bark Oil.
Furfural	trace	trace
1a-Pinene	12-16	75-85
d-Sylvestrene	54-58	—
d-Limonene		
Dipentene	—	5-6
Bornyl acetate	8	1
Free borneol	4	2
"Librocedrene"	6-7	—
"Green oil"	2	3

H. F. E. H.

Comparative Actions of Cane Sugar and Invert Sugar on Alkaline Copper Solutions. L. Maquenne. (*Comptes rend.*, 1916, 162, 145-149.)—The experiments were carried out with 10 c.c. each of the copper and alkaline tartrate solutions, mixed and made up with sugar to a total volume of 36.2 c.c.; the flasks were placed cold in water at the given temperatures, the level of the water being 1 to 2 cm. above that of the liquid in the flasks, and kept immersed for stated times. In the case of invert sugar, for a period of ten minutes, the increase in cupric reduction with increasing temperatures is small and regular from 70° C. upwards, and the influence of variations of 2° or 3° C. is practically negligible. At 65° C. there is a larger difference, and it is preferable either to work at 70° C. or to warm the contents of the flask first to 40° C., or else to keep it in the bath for fifteen minutes instead of ten. In the case of cane sugar the influence of increasing temperatures is relatively very great, and, in order to avoid as far as possible the disturbing effect of cane sugar in the estimation of reducing sugars, it is desirable to work at comparatively low temperatures, preferably at 70° C., at which point the reducing power of cane sugar is 8,000 to 10,000 times less than that of invert sugar, and its influence only one-tenth of what it is at 100° C. Under the conditions noted, the presence of 10 grms. of cane sugar will produce an error of about 1 mgrm. in the estimation of invert sugar. An error of this magnitude may escape detection in methods based on the filtration of the cuprous oxide, but is easily detected by the thiosulphate method. The time of heating has but little influence in the case of invert sugar, except that when working at 65° C. (measured outside) ten minutes is barely sufficient to attain regularity of results. In the case of cane sugar, on the other hand, the reduction

increases largely with the time of heating; and at moderate temperatures with quantities of sugar not exceeding 15 grms., the increase in reducing power is nearly proportional to the time. Hence any sample of sugar, tested at 65° C. under the conditions noted, which shows in twenty minutes a value sensibly less than double that found for ten minutes' heating, contains invert sugar, and this fact may be utilised for the estimation of very small quantities of invert sugar; for instance, 0.5 mgrm. of invert sugar in 10 grms. of cane sugar is clearly shown. At temperatures above 65° C. this proportionality is not so marked. At 100° C. the reduction decreases with increase in the quantity of sugar, whereas at 65° and 70° C. it increases; consequently at some temperature near 100° C. there must be a point at which the reduction is independent of the quantity of sucrose present. The extreme sensitiveness of the reducing power of cane sugar to small changes of temperature may account for variations and errors in results obtained when working at the boiling-point, owing to the fluctuations of barometric pressure. J. F. B.

Estimation of Reducing Sugars in Presence of an Excess of Cane Sugar.

L. Maquenne. (*Comptes rend.*, 1916, 162, 207-213.)—Owing to the appreciable and extremely sensitive cupric reducing power of cane sugar and its influence on the reducing power of the invert sugar itself, certain very elaborate precautions are necessary for the accurate estimation of invert sugar, etc., in presence of an excess of cane sugar. As a general rule, in order to restrict the influence of the cane sugar, the reduction is carried out at a relatively low temperature; the lower the temperature, the longer the time. The absolute minimum is fixed by the author at ten minutes at 65° C. (measured in the water-bath), but even under these conditions the influence of the cane sugar must be determined and accounted for. When working at ebullition (three minutes boiling) the variations of temperature due to barometric pressure may introduce an error up to 0.01 per cent.; this may be compensated by working always against a control experiment made at the same time with pure cane sugar or a sugar of known composition. The ebullition method, in spite of its defects, possesses the advantage that, when an approximation of 1 in 10,000 is sufficient, the same tables may be used as those showing pure invert sugar in absence of cane sugar, since when 10 grms. of sugar are taken at a total volume of 36.2 c.c. the reduction due to the cane sugar is nearly independent of the amount of invert sugar present. In working against a control experiment with pure cane sugar, it is advisable in the analysis of products poor in invert sugar to employ constant quantities—*e.g.*, 20 grms. of cane sugar for each determination at 65° C., or 10 grms. at ebullition—constructing tables for these quantities and making up with pure sugar to the standard quantities whenever it is not convenient to take so much of the original sample. When working at 65° C., or any other temperature which is independent of barometric pressure, a control experiment is not required, and the reduction due to 20 grms. or other standard weight of cane sugar chosen is simply deducted in constructing the tables. Two analytical methods are available: When the amount of cuprous oxide is large, it may be separated by centrifuging or filtration, and estimated by any known accurate method. When the quantity is small, however, an appreciable proportion remains in solution, so that for refined products, poor in invert

sugar, it is essential to proceed by estimating the excess of cupric salt after reduction. For this purpose the author proceeds as follows: Ten c.c. each of copper solution, alkaline tartrate, and water, are mixed, and 10 or 20 grms. of solid sugar dissolved in the mixture; the solution is heated for the prescribed time, cooled, treated with 20 c.c. of 50 per cent. sulphuric acid, 5 c.c. of a 20 per cent. solution of potassium iodide are added, and the titration is made with standardised thiosulphate (20 grms. per litre), using starch paper as an external spot test indicator. The method is not applicable to molasses which contain bodies which combine with iodine. If for any reason the sugar must be dissolved in advance, great care must be taken to avoid the action of the invertase present in many samples of sugar. Especially when working at moderate temperatures, the solution should be cooled and acidified at once to avoid continuation of the reducing action. All the known precautions as to size of vessels, manner of heating, etc., must be closely followed, temperatures must be regulated to 0.5° C., and times to within five seconds; the method being purely empirical and personal, every operator must work with tables constructed by himself. Sugar free from invert sugar may be prepared by three recrystallisations of refined sugar from 75 per cent. aqueous solutions at 90° C.; alcoholic solutions should be avoided. The degree of approximation obtainable when the method is carefully followed is about one-fiftieth of the quantity of invert sugar present—*i.e.*, under favourable conditions, two significant figures exact and the third fairly close, except with less than 1 per cent. of invert sugar, when experimental errors may increase the divergence of the third decimal.

J. F. B.

Presence in Industrial Sugars of Reducing Sugars other than Invert Sugar. L. Maquenne. (*Comptes rend.*, 1916, 162, 277-282.)—The methods now available for the accurate estimation of reducing sugars in presence of a large excess of cane sugar permit closer attention to be paid to those unknown reducing sugars, whether pre-existing in the crude material or formed in the processes of manufacture, traces of which occur even in many refined products. The presence of these reducing sugars, other than invert sugar, is recognised in a general manner by the variation of their cupric reducing power according to the temperature at which the estimation is made. In this respect they resemble cane sugar rather than invert sugar, in that the cupric reducing power increases considerably at ebullition (three minutes at 103° to 104° C. under the conditions prescribed) as compared with that determined at 65° C. (ten minutes' heating in water-bath), whereas the reducing power of invert sugar shows only a slight increase between 65° C. and the boiling-point. Consequently, in the estimation by the author's method of the cupric reducing powers of industrial sugars, by comparison with pure cane sugar, any appreciable difference between the reduction at 65° C. and that at ebullition may be attributed to the unknown reducing sugars. It is true that their influence at 65° C. is probably not absolutely *nil*, and the value attributed to the invert sugar is to that extent over-estimated, but for an approximate and relative measure of the unknown reducing sugars the assumption forms the basis of a useful method. The observations here recorded have two practical consequences: (1) In the examination of the purity of refinery products it is not sufficient merely to determine the invert sugar by cupric reduction at 65° C.;

the total non-cane sugar reducing sugars only exert their full influence at ebullition, and the ebullition test possesses the greatest practical significance. (2) In the examination of sugar products for distillery value the reverse is the case. The unknown reducing sugars are unfermentable, and their estimation leads to an erroneous valuation; the cane sugar and invert sugar alone are of practical significance, and the test at 65° C. should be employed.

J. F. B.

INORGANIC ANALYSIS.

Analysis of Aluminium and its Alloys. W. H. Withey. (*J. Inst. Metals*, 1916, advance proof, pp. 15.)—The paper describes methods for the analysis of alloys of aluminium and copper, of alloys of aluminium and zinc, and of commercial aluminium. The last method is useful for the analysis of alloys of aluminium containing small proportions of magnesium, owing to the fact that large quantities of the alloy may be used in the analysis. In this method use is made of the fact that tartaric acid is capable of preventing the precipitation of aluminium by ammonium sulphide, while at the same time zinc and nickel are precipitated quantitatively. Manganese is only partially precipitated. The filtrate left after the removal of the sulphides produced by hydrogen sulphide in acid solution, and by ammonium sulphide in alkaline tartrate solution, is acidified and concentrated. The solution filtered from sulphur is made ammoniacal, and the magnesium precipitated with sodium phosphate. The precipitate is redissolved, reprecipitated, filtered off, ignited, and weighed. It is then dissolved in nitric acid, and a trace of manganese, usually present, is estimated by a colorimetric method, and the equivalent amount of manganese pyrophosphate calculated. This amount is deducted from the weight of "magnesium pyrophosphate" previously found. The manganese in the alloy is estimated in a separate portion.

The method recommended for the analysis of alloys of aluminium and zinc consists in adding to the solution an excess of caustic soda. The hydroxides first precipitated are thus dissolved, and on passing hydrogen sulphide through the solution zinc is precipitated. The precipitate is redissolved, and the zinc, after removal of traces of aluminium, is determined as phosphate.

Test analyses show that the methods described are very satisfactory. The methods are described in detail in the paper, which should be consulted by those wishing to use them.

G. C. J.

Rapid Method for the Estimation of Copper and Iron. G. Edgar. (*J. Amer. Chem. Soc.*, 1916, **38**, 884-887.)—A modification of Volhard's method for the estimation of copper is described, by which copper and iron may both be estimated in the same solution, the copper being precipitated as cuprous thiocyanate by standard ammonium thiocyanate solution, and the iron titrated with permanganate solution. The solution containing the copper and iron, together with some sulphuric acid, is neutralised with ammonia, saturated with sulphur dioxide, heated just to boiling, and standardised ammonium thiocyanate solution is added in quantity sufficient to precipitate all the copper. Usually the iron is not completely reduced at this point, and a red colour of ferric thiocyanate persisting for a few minutes indicates that the copper

has been precipitated completely. The mixture is now boiled for ten minutes while a current of carbon dioxide is passed into it; this serves to remove the last traces of sulphur dioxide. The current of carbon dioxide is continued while the mixture is being cooled, the precipitate then collected on a filter and washed with cold water. The filtrate is acidified with a few c.c. of dilute sulphuric acid, a quantity of standardised silver nitrate solution is added sufficient to precipitate the excess of thiocyanate, and the iron is titrated with permanganate solution in the usual way. A trace of ferrous sulphate is added to destroy the slight excess of permanganate, and the excess of silver in the solution is titrated with thiocyanate solution. If iron is not present, it will be necessary to add ferric sulphate to act as indicator in the latter titration. The quantity of iron present is calculated from the volume of permanganate used; the copper is found from the difference between the total volume of thiocyanate solution added and the volume equivalent of the silver nitrate solution used (1 c.c. of $\frac{N}{10}$ thiocyanate solution corresponds with 0.006357 grm. of copper). In dealing with quantities of copper varying from 0.03 to 0.16 grm. and of iron from 0.02 to 0.25 grm., the maximum error for either metal is ± 0.0002 grm.

The method is particularly suited to the estimation of copper and iron in ores. The sample is decomposed with concentrated nitric and hydrochloric acids in the usual way, and then heated with sulphuric acid until the former acids have been expelled; after the solution thus obtained has been diluted with water, it is ready for treatment as described. The insoluble residue need not be separated. Ores which are not decomposable by acid treatment must be subjected to fusion methods. If silver is present, the silver chloride must be separated before the solution is heated with sulphuric acid.

W. P. S.

Detection of Free Chlorine in Town Service Waters. G. A. Le Roy. (*Comptes rend.*, 1916, 162, 327-329.)—For the sterilisation of potable waters the addition of hypochlorites is extensively practised by public supply authorities, the average proportion used (in France) being equivalent to about 0.8 mgrm. of active chlorine per litre of water. Although the major portion of the hypochlorite rapidly disappears as the result of its action, any excess may be disagreeable or even harmful to the consumer, and a proportion amounting to about 0.05 mgrm. of active chlorine per litre is perceptible to the palate. This proportion corresponds with the limit of sensitiveness of the starch-iodide test, and some more delicate method is desirable for the analytical examination of such waters. The author proposes to effect the concentration of the active chlorine present in the water by a process of fractional refrigeration. If the usual reagents have shown negative results, a suitable quantity of the water—*e.g.*, 10 litres—is exposed in a metal, preferably enamelled, vessel to a gradual freezing process, care being taken not to produce any unnecessary aeration by vigorous stirring. When only about one-fiftieth of the original quantity of water remains in the liquid condition, this is removed and tested with the starch-iodide reagent. In this way a quantity of 0.0005 mgrm. of active chlorine per litre of original water may be detected. If preferred, the water may be frozen solid and the test applied to the central core of the block of ice split longitudinally. The reaction may be made approximately quantitative by colorimetric comparison. J. F. B.

Use of Copper Oxide for Fractionation Combustion of Hydrogen and Carbon Monoxide in Gas Mixtures. G. A. Burrell and G. G. Oberfell. (*J. Ind. and Eng. Chem.*, 1916, 8, 228-231.)—The authors recommend the use of copper oxide, heated to between 275° and 300° C. for the combustion of hydrogen and carbon monoxide in gas mixtures. Experiments are described which show that combustion of hydrogen and carbon monoxide is complete at 290° C., whilst methane and higher paraffins are unaffected. A suitable combustion-tube and electrical furnace are figured in the paper. G. C. J.

Reagents for Use in Gas Analysis. II. Chromous Chloride. R. P. Anderson and J. Riffe. (*J. Ind. and Eng. Chem.*, 1916, 8, 24-26.)—Chromous chloride is stated to be of use for the absorption of oxygen in the presence of carbon dioxide and hydrogen sulphide where other reagents cannot be employed. It was found impossible to prepare it in the form of a stable solution by the methods followed by Otto von der Pfordten and by Jannasch and Meyer, all of whom prepared chromous chloride by decomposing chromous acetate with hydrochloric acid. The preparation of chromous chloride by the reduction of violet chromic chloride at a temperature of 400° to 500° C. by means of hydrogen results in a solution which when filtered through glass wool is stable, but its absorption of oxygen, although rapid, is not quite complete, and therefore the reagent thus prepared is unsatisfactory for gas-analytical work. The authors consider, however, that it is not proved that a solution of this substance which would be suitable cannot be prepared, though in view of the high cost of materials and the inconvenience of preparation it is likely to have but a restricted application.

H. F. E. H.

Reagents for Use in Gas Analysis. III. Specific Absorption of Alkaline Pyrogallol in Various Pipettes. R. P. Anderson. (*J. Ind. and Eng. Chem.*, 1916, 8, 131-133.)—The author has previously shown that this reagent is best made up by dissolving 15 grms. of pyrogallol in 100 c.c. of potassium hydroxide solution of sp. gr. 1.55 (*ANALYST*, 1915, 40, 409). It is now shown that, when a reagent of this composition is employed, Orsat's original pipette is to be preferred to any of the other pipettes which have been designed for use without shaking—for example, the pipettes of Hankus, Nowicki-Heinz, and Dennis. The inefficiency of the Orsat pipette with the weaker solutions of alkaline pyrogallol usually employed is well known, and the reason why the other pipettes referred to were designed; and the author concludes that it is the greater viscosity of his solutions which increases the efficiency of the Orsat pipette. One-minute contact with the reagent in an Orsat pipette serves to remove the whole of the oxygen from 100 c.c. of air, and the speed of the reaction does not fall until the reagent has absorbed more than twenty times its volume of oxygen. The oxygen in commercial oxygen cannot be entirely removed by the use of any of the pipettes designed for use without shaking, and another form of pipette must be used for such purposes. The sole disadvantage of the ordinary Orsat pipette for the analysis of gases with 20 per cent. or less oxygen is that a deposit which forms gives a good deal of trouble with this form of pipette. Slight

modification of the pipette, however, overcomes this difficulty, and a modified pipette which serves well is described on page 190. G. C. J.

Estimation of Iodine and Bromine in Saline Waters. D. E. Popa. (*Bull. Sci. Acad. Romana*, 1915-16, 4, 308-317.)—The method proposed is a modification of one described previously by Weszelszky, which depends on the oxidation of the iodine to iodic acid by means of chlorine in acid solution, the bromine at the same time being liberated and separated by distillation. A small quantity of the bromine is, however, converted into bromic acid, and the modification of the method enables this quantity to be recovered by means of a double treatment with chlorine and an intervening reduction. One hundred c.c. of the water are rendered alkaline with sodium hydroxide, evaporated, and the residue is ignited at a low temperature in order to destroy organic substances. The residue is then taken up with water, the solution filtered, the insoluble portion washed with water, and the filtrate and washings evaporated to about 70 c.c. This solution is transferred to a distillation flask, acidified with sulphuric acid or hydrochloric acid, 75 c.c. of 1 per cent. chlorine solution are added, and the mixture is distilled into a receiver containing 1 per cent. potassium hydroxide solution; a current of carbon dioxide is passed through the apparatus when steam begins to enter the receiver. After about thirty minutes' distillation, the contents of the flask are cooled, 20 c.c. of saturated sulphur dioxide solution are added, and the mixture is boiled until practically all the sulphur dioxide has been expelled; the receiver is meanwhile detached, the alkaline solution transferred to a porcelain basin, and a fresh quantity of potassium hydroxide introduced. The solution in the flask is then treated with chlorine and the distillation repeated. The united alkaline distillates (containing the hypobromite) are evaporated, the residue is heated on a boiling water-bath for forty-five minutes, then dissolved in 130 c.c. of water, the solution is treated with potassium iodide and sulphuric acid, and the liberated iodine titrated in the usual way; the quantity of iodine is a measure of the bromine. Small amounts of chlorate which may be present do not interfere at the dilution given. The solution remaining in the distillation flask is boiled for about fifteen minutes to remove a trace of bromine which remains (this quantity of bromine is too small to affect the bromine result, but interferes with the iodine estimation), then cooled, potassium iodide is added, and the liberated iodine is titrated. W. P. S.

New Methods for Analysis of Lime-Sulphur Solutions. R. M. Chapin. (*J. Ind. and Eng. Chem.*, 1916, 8, 151-156.)—The author expresses the view that the important problem in connection with the analysis of these cattle-dipping solutions is to determine the balance between the positive and negative constituents—that is, to ascertain quantitatively whether a solution contains excess lime or excess hydrogen sulphide.

He estimates the "total (sulphide) base," whether existing as sulphide, hydroxide, or hydroxysulphide, by titration with mineral acid, using methyl orange as indicator with fresh solutions, and sodium nitroprusside with dirty solutions which have been used. Concentrated commercial preparations are diluted to the strength used for dipping

(1.5 to 2 per cent. "sulphide sulphur"), and 10 c.c. of this dilution are delivered into 30 c.c. of water, titrated with $\frac{N}{10}$ hydrochloric acid until the yellow tint has gone, when 1 drop of dilute methyl orange solution is added and the titration completed. This method is not available with dirty, used solutions. Of these, 10 c.c. are diluted with 30 c.c. water and titrated with $\frac{N}{10}$ acid until the yellow colour becomes faint. A drop of liquid is treated on a spot plate with a drop of a freshly prepared 0.2 per cent. solution of sodium nitroprusside. If a violet colour appears quickly, the titration is continued. When the development of colour is slow or doubtful, one of the cups in the spot plate is filled with the solution and a drop of nitroprusside solution added. Two further additions of $\frac{N}{10}$ acid are made, and a portion of the solution withdrawn after each addition and tested in a similar manner. After fifteen minutes the spot tests are examined, the end of the titration being indicated by a dirty green turbidity, in no way resembling the former clear violet. This first titration fixes the end-point approximately, and in subsequent titrations smaller additions of acid are made after the withdrawal of the first and second test portions.

Next the "reaction figure" is determined. This is the measure of the apparent free hydroxide or free hydrogen sulphide. The method depends on the fact that tetrathionate reacts with sulphides, with the formation of thiosulphate and separation of sulphur. Sulphides being thus eliminated, hydroxide can be titrated with the use of the ordinary indicators appropriate for moderately strong acids. The reaction between tetrathionate and sulphides progresses normally only in alkaline solutions. On the other hand, alkalis decompose tetrathionates, with production of acidity. This is avoided by working in weak ammoniacal solution, which has a negligible effect on tetrathionate. Into a 250 c.c. flask is introduced a sufficient excess of $\frac{N}{10}$ iodine solution (about 25 per cent. more than the volume of $\frac{N}{10}$ acid required in estimating "total sulphide base"). $\frac{N}{10}$ thiosulphate is next added until the colour is nearly discharged. A little $\frac{N}{10}$ hydrochloric acid is added to destroy any iodate, and then thiosulphate, drop by drop, until the colour is finally discharged. About 5 c.c. of 10 per cent. ammonium chloride are added, the mixture diluted to 100 c.c., 1 drop of methyl red indicator (0.2 per cent.) added, then $\frac{N}{10}$ caustic soda to faint alkalinity, and finally $\frac{N}{10}$ hydrochloric acid, until the return of a distinct orange colour. To this neutral solution of tetrathionate 10 c.c. of $\frac{N}{10}$ caustic soda and 10 c.c. of the sample are added. The flask is stoppered and the mixture allowed to stand for three minutes. One more drop of methyl red solution is added, and the mixture titrated with $\frac{N}{10}$ hydrochloric acid to a distinct end-point. If the original solution was neutral, 10 c.c. of acid will be required. If more or less than 10 c.c. be required, the difference from 10 c.c. is the "reaction figure," and is regarded as positive or negative respectively. This method is only available with unused material. In such cases the author's third figure, the "sulphide acid figure," is given by subtracting the reaction figure from the sulphide base figure.

With dirty solutions, the sulphide acid figure is determined directly by the following method and the reaction figure calculated: The method consists in titrating an ammoniacal dilution of the sample with $\frac{N}{20}$ tetrathionate until an appropriate indicator no longer shows a trace of sulphide remaining. The $\frac{N}{20}$ tetrathionate is freshly prepared from $\frac{N}{10}$ iodine and $\frac{N}{10}$ thiosulphate. Into 10 c.c. of dilute (1:10)

ammonia, 10 c.c. of the lime sulphur solution are added, and tetrathionate is added from a burette until the yellow tint becomes faint. For finishing the titration a 1 per cent. solution of nickel sulphate is used as outside indicator. One drop of the indicator is put on the plate first, and then enough of the solution under titration to fill the cup if colour does not appear with the first drop. The end-point, passing from faint grey to faint bluish-green, is sharper than any the author has been able to obtain with any indicator when a metallic salt solution is used as the titrating agent. To the volume of tetrathionate solution required a constant correction of 0.2 c.c. is added.

G. C. J.

Estimation of Moisture in Syrups by the Calcium Carbide Method. R. M. West. (*J. Ind. and Eng. Chem.*, 1916, **8**, 31-35.)—The apparatus employed is a modification of that described by McNeil (*ANALYST*, 1912, **37**, 475), and differs (1) in the form of generating flask, to which a stirring device has been added; and (2) in the introduction of a drying tube, containing calcium chloride, between the gas burette and the generating flask as protection against too high yields of acetylene due to the action of the water vapour from the burette. Admixture of barium sulphate or silica, as recommended by McNeil (*loc. cit.*), was found unsatisfactory, since moisture is lost from the material under examination by evaporation during the admixture of the inert material. It was found essential to the process that the carbide and material to be tested should be thoroughly mixed within a closed container, and this the present apparatus provides means for doing. About 25 grms. of carbide are used, and from 5 to 10 grms. of the sample, the carbide being added by degrees, with thorough mixing in the special chamber. The equivalent found was 1 c.c. of acetylene for every 0.001725 grm. of water, McNeil's value being 0.001718. The method is found to be accurate within three- or four-tenths of a per cent., and is more rapid than the A.O.A.C. official method, in which sand or pumice is used, and can be used for fruit juices when acids are present by correcting the volume of acetylene for the total acidity.

H. F. E. H.

Comparative Study of Aeration and Heat Distillation in the Kjeldahl Method for the Estimation of Nitrogen. K. G. Falk and K. Sugiura. (*J. Amer. Chem. Soc.*, 1916, **38**, 916-921.)—The aeration method of distilling ammonia (*cf.* *ANALYST*, 1913, **38**, 580) frequently gives low results, and should not therefore be used. In experiments with hexamethylenetetramine, uric acid, glycylglycine, alanyl-glycine, glycine, alanine, and urea, the quantities of nitrogen found by the aeration method were from 0.30 to 1.97 per cent. lower than the amounts obtained by ordinary distillation. When the liquid remaining after the aeration process was distilled, an additional quantity of nitrogen was obtained, and this, added to the amount found by aeration, gave a total which agreed closely with the ordinary distillation result. The aeration method also gave low results when applied to pure ammonium sulphate.

W. P. S.

Estimation of Citrate-Soluble Phosphoric Acid in Basic Slag by the Iron Citrate Method. M. Popp. (*Chem. Zeit.*, 1916, **40**, 257-260.)—Commercial ferric

chloride varies considerably in composition (samples examined by the author contained from 58.8 to 99.6 per cent. of actual ferric chloride), but the iron citrate solution, recommended for use in preventing the interference of silica in the estimation of phosphoric acid (*cf.* ANALYST, 1913, 38, 526), will contain a quantity of iron sufficient for the purpose even when the solution is prepared with ferric chloride of poor quality. The hydrogen peroxide solution used in the process keeps its strength for a considerable time if 0.005 per cent. of acetanilide is added to it; 0.5 per cent. of alcohol has the same preservative effect. The quantity of hydrogen peroxide solution employed should not exceed 3 c.c.; a larger quantity causes the result (for phosphoric acid) to be too low. This takes place only when dealing with basic slag, and not with pure phosphate solutions mixed with manganese and calcium salts; some constituent (possibly silica) of the basic slag evidently produces the effect.

W. P. S.

Comparison of Methods for Estimation of Phosphates in Soils. W. O. Robinson. (*J. Ind. and Eng. Chem.*, 1916, 8, 148-151.)—The fusion method is fairly satisfactory, but is subject to one inherent error—namely, the solubility of small amounts of ammonium phosphomolybdate in aqueous solutions of sodium nitrate. In presence of sufficient alumina or ferric oxide the phosphoric acid can be precipitated with these, and separation from sodium nitrate made in this way. This introduces an additional operation, and, except for very small percentages of phosphoric acid, is unnecessary.

Washington's method (*Chemical Analysis of Rocks*, p. 162) is the best method yet described, but requires an abundant supply of platinum apparatus. The soil is first evaporated with nitric acid, and ignited to destroy organic matter, taking care that there is no glowing during ignition. Any siliceous envelope in which particles of apatite may be enclosed is then removed by treatment with hydrofluoric acid.

Fischer's method (*Intern. Mitt. f. Bodenkunde*, 1913, 2, 541) is rather more troublesome, but avoids the necessity for platinum apparatus, and brings all but a negligible trace of phosphorus into solution. It consists in digestion with *aqua regia*, followed by evaporation to dryness, ignition, and subsequent treatment with nitric acid.

Vanadium interferes with the phosphorus determinations in soils. This influence can be avoided by reducing the vanadium with ferrous sulphate and precipitating at low temperatures by shaking (*cf.* Cain and Tucker, ANALYST, 1913, 38, 478). With soil solutions it is not necessary to add sulphurous acid to prevent re-oxidation of the vanadyl salt. The influence of vanadium is also avoided by using the gravimetric method, provided precautions are taken for complete precipitation and the ammonium-magnesium phosphate precipitate is not allowed to stand too long.

Tungsten and titanium do not interfere with the estimation of phosphorus in soils by the gravimetric method, provided precautions are taken to make the precipitation complete.

G. C. J.

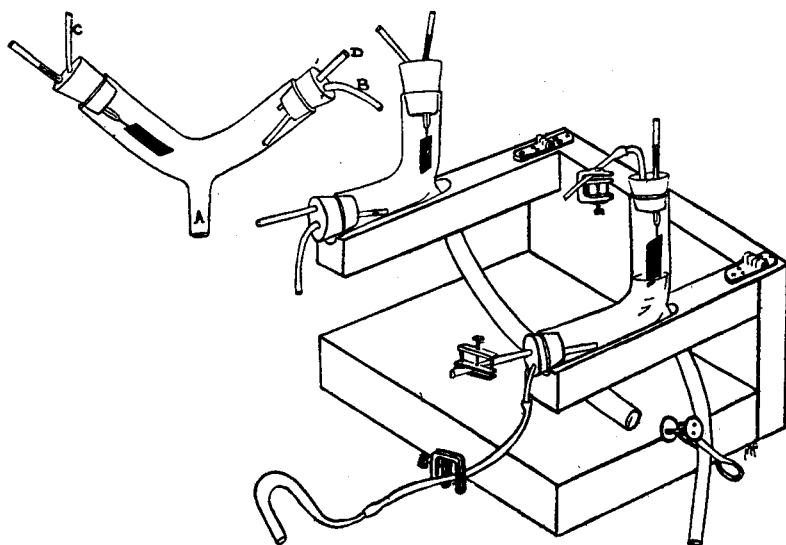
Estimation of Zinc by Electrolysis. F. Chancel. (*Bull. Soc. Chim.*, 1916, 19, 59-63.)—The zinc (about 0.3 grm.) is dissolved in 1.5 grms. of sulphuric acid and

about 2 grms. of nitric acid, the solution evaporated on the water-bath, and the residue heated in the air-bath to expel nitric acid. The zinc sulphate is dissolved, and the solution neutralised with ammonia, with methyl orange as indicator, and then acidulated with 0.25 c.c. of $\frac{N}{2}$ sulphuric acid, and treated with 0.2 gm. of sodium formate for each 0.1 gm. of zinc present. The solution is electrolysed with a current of 4 to 5 amperes per square decimetre of cathode surface, which is preferably of sheet platinum, while the anode consists of platinum wire. During the electrolysis the vessel should be cooled in water, and the deposition of zinc will be complete in two to three hours. The deposits are rendered more complete and adherent by amalgamating the cathode with not less than 0.3 gm. of mercury deposited by electrolysing an acid solution of mercuric nitrate. In applying the method to brass, about 0.5 gm. of the metal is dissolved in nitric acid, the copper precipitated, and the filtrate evaporated with 1.5 gm. of sulphuric acid to expel all nitric acid. The iron is precipitated with ammonia, the excess of which is expelled by boiling, the liquid then neutralised with sulphuric acid, and the zinc precipitated electrolytically as described.

C. A. M.

APPARATUS, ETC.

Simple Cell for the Determination of Hydrogen Ion Concentration.
J. H. Long. (*J. Amer. Chem. Soc.*, 1916, **38**, 936-939.)—The cell consists of a Y-tube having a capacity of about 15 c.c.; about 5 c.c. of liquid are used in each test, the remainder of the space being occupied by the hydrogen. The liquid is admitted

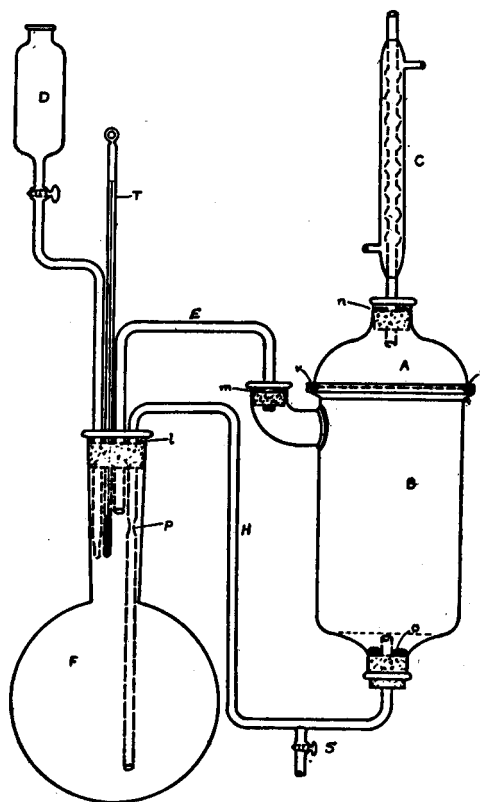


through the tube *A* (see figure on the left), and flows out at *B*. The wide branches of the Y-tube are closed by rubber stoppers carrying two holes, the exposed surfaces being coated with paraffin. A small glass tube filled with mercury passes through one of the holes, and is connected with the platinised electrode by means of a platinum wire. The washed hydrogen passes through from *D* to *C*, which are very

narrow tubes. Rubber tubes over the ends of these are fitted with screw-clamps, so that the flow of hydrogen may be regulated. The liquid exit tube is connected by a capillary, extended into a wider tube, with the bridge intermediary vessel containing 3.5 N potassium chloride solution, and connected in turn with the calomel electrode. A pair of such cells is shown mounted for use (right-hand figure); the hinged supports allowed the cells to be inclined in order to regulate the depth to which the platinum is immersed in the liquid. The arrangement also provides for the rapid agitation of the liquid and gas mixture. Constant readings are obtained in about ten minutes after filling with liquid and hydrogen and agitating. The apparatus has been tested in comparison with Hasselbalch cells and by the use of liquids of known hydrogen ion concentration; the final results were the same in cases where an accuracy of 0.5 millivolt was sufficient.

W. P. S.

Large Fat Extractor. C. L. A. Schmidt. (*J. Ind. and Eng. Chem.*, 1915, 8, 165.)—The extractor illustrated is not designed for the estimation of fat, for which purpose older extractors serve well, but for the preparation of large quantities of fat-



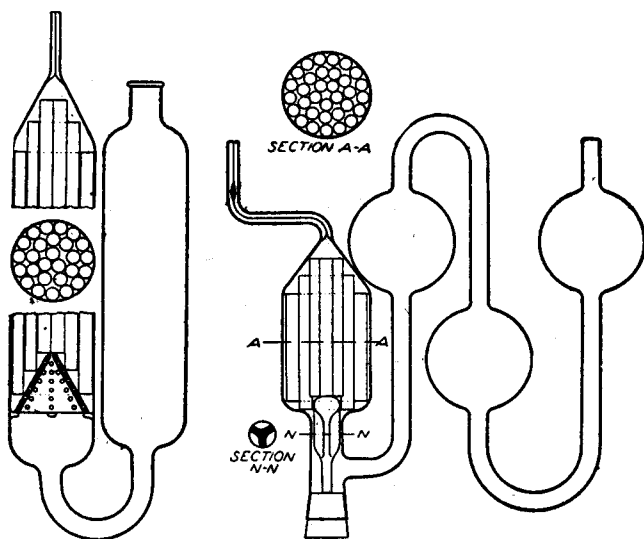
free material. The illustration is self-explanatory if it be noted that the joints at *v*, *l*, *m*, *n*, and *o* are mercury-sealed to prevent loss of ether vapour.

G. C. J.

New Penetration Needle for Use in Testing Bituminous Materials. C. S. Reeve and F. P. Pritchard. (*J. Agric. Research*, 1916, 5, 1121-1126.)—A standard needle for use in Richardson's "penetrometer" and other machines for testing the softness of bituminous materials may be prepared from a 2-inch length of 0.041-inch annealed steel drill rod, which is fixed in the chuck of a lathe and ground by means of a file to a sharp point tapering $\frac{1}{4}$ inch from the end. It is then tempered, ground on a stone, polished with emery-powder, crocus cloth and rouge, and finished on a buffing wheel. The tempering solution consists of salt (650 grms.), nitre (170 grms.), powdered alum (100 grms.), and mercuric chloride (20 grms.), in 10 gallons of water. The needle is heated to dull white heat and plunged into the liquid, then lightly cleaned with emery cloth, heated to below dull redness, and again plunged into the solution. The finished needle must have a perfectly straight taper $\frac{1}{4}$ inch from the end. Its point must be sharp enough to pierce writing paper without sticking, and its diameter above the taper must be exactly 0.04 inch.

C. A. M.

Pipettes especially adapted for Use with Alkaline Pyrogallol. R. P. Anderson. (*J. Ind. and Eng. Chem.*, 1916, 8, 133-135.)—These pipettes are designed to overcome the difficulties attendant on the formation of a precipitate in alkaline pyrogallol. The construction of the modified Orsat pipette and of the other



pipette intended to be mounted separately in a frame is clearly shown in the illustration. The cone supporting the glass tubes shown in the figure is of perforated porcelain. Attention is also directed to the pronounced conical upper end of the pipettes.

G. C. J.

Reagents for Use in Gas Analysis. IV. Phosphorus in Solution. R. P. Anderson and W. Biederman. (*J. Ind. and Eng. Chem.*, 1916, 8, 135-136.)—A solution of phosphorus in castor oil fails to remove the whole of the oxygen from air, even with nine minutes' shaking at 25° C. G. C. J.



REVIEWS.

REPRESENTATIVE PROCEDURES IN QUANTITATIVE CHEMISTRY. By FRANK AUSTIN GOOCH. London: Chapman and Hall, 1916. Pp. 262. Price 8s. 6d. net.

From almost any other writer an excuse would be expected for adding to the list of students' textbooks on quantitative analysis (inorganic chemistry), but Professor Gooch's reputation disarms such a challenge. The book is—to quote from the preface—the “outgrowth of long experience in the teaching of the subject,” and this is evident in the many valuable directions and precautions offered in describing common methods of analysis; it is also a commendable feature of the book that even standard methods of analysis are represented to be only relatively efficient, and that to secure maximum accuracy there should always be an intelligent regard for the limitations of the method selected. The habit of critically regarding the method thus inculcated should prove valuable to the student.

The statements of principles and the directions are ample, and the general text of the book is conspicuously free from slips. Some reservation of this statement is, however, necessary in connection with reaction equations, several of which do not “balance,” or otherwise show a want of final revision. In view of future editions we would draw the author's attention to the following equations which thus need revision: Pp. 4 (bottom), 93 (top), 138, 141 (bottom), 143 (bottom), 152 (top), 154 (top), 165 (top), 170 (top), 184 (top), and 206 (bottom). On p. 135, in the determination of H_2O_2 by $KMnO_4$ titration, we are directed to titrate a 0.001 per cent. strength of H_2O_2 with $\frac{N}{10} KMnO_4$. But could this be done satisfactorily? One hundred c.c. of the dilute H_2O_2 solution would only require about 0.6 c.c. of $\frac{N}{10} KMnO_4$.

Exception must be taken to one habit of expression in the book: we refer to the evidently deliberate way in which Professor Gooch cubes all his volumes. This deserves at least some explanation, for the disadvantages are clear, whilst no counter-advantages are to be seen. The normal use of the index number to indicate the power to which a quantity is to be raised is evidently not abandoned, for on p. 63 we find it stated that “ $(\frac{1}{2})^4 = \frac{1}{16}$,” and that “ $(\frac{1}{10})^4 = \frac{1}{10,000}$.” On p. 56 we are told that “2 amp. of current may be applied successfully to 2 cm.² of cathode surface.” By common acceptance the “2 cm.²” would mean 4 sq. cm.; but, a page or two before, we find an ordinary cathode exposing about “30 cm.²” of surface, and here it is obvious from the context that what is meant is not 900 sq. cm., but 30 sq. cm.

And when we come to volumes, the sign of the cube is *invariably* used; thus 100 c.c. is given as "100 cm.³," 2.05 c.c. as "2.05 cm.³," 1 litre as "1,000 cm.³," and so on. The mind is given a jolt each time it rides over one of these expressions, and one is at a loss to see what benefit accrues. This is our one serious complaint against the book.

The work is divided into five chapters, the titles of which indicate the contents. Chapter I., "Processes of Analysis;" Chapter II., "Processes of Weighing and Measuring;" Chapter III., "Procedures in Gravimetric Analysis;" Chapter IV., "Procedures in Volumetric Analysis;" and Chapter V., "Systematic Analysis."

In dealing with the fundamental principles and appliances of quantitative analysis there is not much scope for novelty of matter, but the treatment is fresh and sound. One instance may be given to show how the student's mind is kept alert as to the properties of solutions. In connection with the tendency of the larger crystals to grow in size at the expense of the smaller crystals when both are in contact with their saturated mother liquor, it is stated that the solubility of a substance is determined by the *size* of the crystal, and, as illustrating this, that calcium sulphate, if reduced to particles of not less than 0.002 mm. diameter, has a solubility of 2.085 grms. in 1 litre, whereas if the particles are of about one-tenth the above diameter, the solubility at the same temperature is increased to 2.476 grms. per litre.

The personal preferences of a well-known teacher of chemistry are always interesting, and these we think we may detect in the section dealing with "Iodometric Processes." It takes up more than a fifth of the book, and the ingenuity with which Professor Gooch applies the iodine interactions is almost uncanny. Give him the usual iodimetric solutions, and he shows you how to determine sulphites, thiosulphates, sulphides, bromine and chlorine, iodates and periodates, iodides, hydrogen peroxide, hypochlorites, bromates, chromates, lead dioxide, cerium dioxide, gold trichloride, ferric chloride, copper, arsenic, antimony, vanadium, molybdenum, cerium, selenium and tellurium, manganese dioxide, chlorates, nitrates, nitrites, hydrochloric acid, sulphuric acid, boric acid, aluminium sulphate and aluminium chloride, nickel and cobalt sulphates, alkaline hydroxides and alkaline carbonates, and even this does not exhaust the list; often alternative iodometric processes are given.

The analyst instinctively prefers making use of reactions that are specific rather than general, and the very universality of a method of analysis implies its limitations. Nevertheless, this section will prove decidedly valuable for reference. A drawback in connection with iodometric analysis is the instability of the standard solutions. We have not noticed in the book a reference to the very convenient method of ascertaining their strengths by means of the almost permanently stable standard $K_2Cr_2O_7$ solution. A definite volume of this, to which an excess of HCl and KI solution has been added, liberates an equivalence of iodine, which can be used in ascertaining the strength of a thiosulphate solution.

The work may be safely recommended to students; perhaps a want of balance is evident in the space allotted to iodometric processes, but in this respect it gains in

value for the general analyst, by whom the book may often be referred to with advantage.

A word of praise is due to the publishers for the general "get-up" of the book.

J. H. B. JENKINS.

ORGANIC CHEMISTRY, OR THE CHEMISTRY OF THE CARBON COMPOUNDS. By VICTOR VON RICHTER. Edited by PROFESSOR R. ANSCHÜTZ and PROFESSOR G. SCHROETER. Volume I.: Chemistry of the Aliphatic Series. Newly translated and revised from the German Edition of 1909 (after Professor Edgar F. Smith's Third American Edition), by Percy E. Spielmann, Ph.D., B.Sc., F.I.C., A.R.C.Sc., 1916. Price 21s. net. Published by Kegan Paul, Trench, Trübner and Co., Ltd.

Organic Chemistry still expands, and with little consideration for the writers of advanced textbooks. Nevertheless a prodigious volume of material has now taken a shape which can be regarded with some confidence as final, and the editors who have collected and systematised this matter as it stood in 1909 and finally condensed it with such discrimination in the space occupied by the last German edition of Richter's textbook deserve the thanks of all chemists. Certain sections of the book, such as those on the sugars and on the derivatives of uric acid, are fairly exhaustive. But the work is no mere collection of monographs, being rather an abridged dictionary of the Science of Organic Chemistry; the reviewer has found it indispensable for reference as an adjunct to Beilstein's "Handbuch" and Richter's "Lexikon," the former of which in many particulars is now so lamentably out of date.

The volume under review is the first of two into which the English edition, following the original plan, is divided. It opens in the conventional manner with brief descriptions of general laboratory methods for determining the composition and physical properties of carbon compounds, and with an outline of the theoretical basis of structural Organic Chemistry, the bulk of the book being devoted to the descriptive chemistry of the aliphatic compounds.

Had Dr. Spielmann undertaken to make any serious departure from the original text, he would doubtless have dwelt at greater length on contact methods at high and low temperatures. In this department of the science great strides have been made during the last few years, and it is here that the book least accurately reflects our present-day knowledge. The work is, for the most part, a faithful but by no means slavish translation of the German; some corrections have been found necessary, in connection with which there is evidence that the translator has frequently consulted original memoirs. Great care has been exercised with the large number of constitutional formulæ, and comparatively few, if any, errors have crept in. The text is free from the students' colloquialisms which so frequently disfigure English and American works on Organic Chemistry.

The small type which forms so substantial a part of the work is not so

clear as in the German edition, nor is the binding or paper quite so attractive. These, however, are only defects by comparison, and the book is one which should certainly prove of great value to all organic chemists who do not already possess the original, or who for any reason prefer an English presentation.

ARTHUR LAPWORTH.

AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS. BY EMIL HATSCHKE.

London: J. and A. Churchill. Second Edition, 1916. Price 3s. net.

This is a second edition of Mr. Hatschek's little book, of which the writer has already had the opportunity of expressing his appreciation. The only substantial addition to the text consists of an appendix, in which the author has given a short account of certain apparatus and procedures employed in the investigation of colloids. This appendix undoubtedly adds to the usefulness of the book, but it might with great advantage have been more expanded, only about ten pages being devoted to the Jentzsch condenser, ultra-filters, apparatus for coagulation tests, and the preparation of gelatin, agar, and silicic acid sols.

Every branch of chemistry has its own methods and its own technique, and it is greatly to be hoped that one day Mr. Hatschek will add to the boon which he has already conferred upon chemists by undertaking the preparation of a laboratory handbook in connection with the study of the colloidal state of matter. The subject is one of great and increasing importance, and no one is better qualified than Mr. Hatschek to undertake the task.

A. CHASTON CHAPMAN.