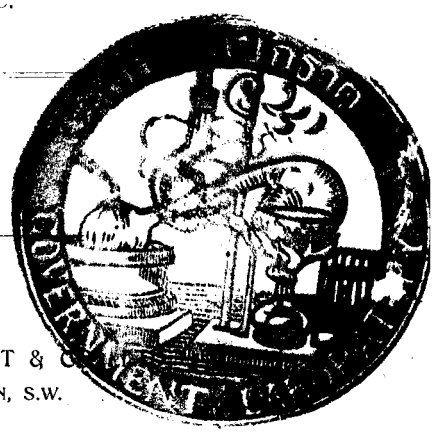
THE ANALYST:

THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF ANALYTICAL CHEMISTRY



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THE ANALYST.

INTERNATIONAL ATOMIC WEIGHTS, 1916.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·88	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·005	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·4
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	88·7
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

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

AN ordinary meeting of the Society was held on Wednesday evening, December 1, in the Chemical Society's Rooms, Burlington House. The President, Mr. A. Chaston Chapman, F.I.C., occupied the chair.

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

Certificates of proposal for election to membership in favour of Messrs. T. F. Harvey, C. H. Manley, B.A., A.I.C., C. C. Roberts, M.A., A.I.C., and F. T. Shutt, M.A., D.Sc., F.I.C., were read for the second time; and certificates in favour of Mr. Nelson Trafalgar Foley, The Nook, Claygate, Surrey, assistant manager and chemist to Messrs. Loders and Nucoline, Ltd., Hammersmith, and Mr. Thomas John Hitchcock, 28, Albany Road, Manor Park, Essex, chief chemist to the Sugar and Malt Products Co., Ltd., Stratford, were read for the first time.

Messrs. A. S. Carlos, B.Sc., A.I.C., and E. K. Rideal, B.A., Ph.D., A.I.C., were elected members of the Society.

The President announced the Council's nominations of Officers and Council for 1916 as follows:

President.—G. Embrey, F.I.C.

Past-Presidents serving on the Council (limited by the Society's Articles of Association to eight in number).—L. Archbutt, F.I.C.; E. J. Bevan, F.I.C.; A. Chaston Chapman, F.I.C.; Bernard Dyer, D.Sc., F.I.C.; Otto Hehner, F.I.C.; R. R. Tatlock, F.I.C.; E. W. Voelcker, A.R.S.M., F.I.C.; J. Augustus Voelcker, M.A., B.Sc., Ph.D., F.I.C.

Vice-Presidents.—Harold G. Colman, M.Sc., Ph.D., F.I.C.; J. H. B. Jenkins; R. T. Thomson, F.I.C.

Hon. Treasurer.—E. Hinks, B.Sc., F.I.C.

Hon. Secretaries.—P. A. Ellis Richards, F.I.C.; E. Richards Bolton.

Other Members of Council.—W. T. Burgess, F.I.C.; J. A. Dewhirst, F.I.C.; J. T. Dunn, D.Sc., F.I.C.; P. V. Dupré, A.C.G.I., F.I.C.; R. G. Grimwood, F.I.C.; H. G. Harrison, M.A., F.I.C.; E. M. Hawkins, F.I.C.; A. W. Knapp, B.Sc., F.I.C.; S. J. C. G. Macadam, F.I.C.; W. Macnab, F.I.C.; H. L. Smith, B.Sc., F.I.C.; W. Collingwood Williams, B.Sc., F.I.C.

The following papers were read: "Formic Acid as a Reagent in Essential Oil Analysis," by W. H. Simmons, B.Sc.; "The 'Presumptive Coli Test' on Unchilled Water," by W. Partridge, F.I.C.; and "Notes on Methods of Analysing Oleaginous Seeds and Fruits," by E. Richards Bolton.

NOTE ON THE MELTING-POINT OF SALICYLIC ACID, AND A TEST FOR THE PRESENCE OF PARA-HYDROXYBENZOIC ACID.

By Henry L. Smith, B.Sc., F.I.C.

(*Read at the Meeting, November* 3, 1915.)

In the examination of some proprietary derivatives of salicylic acid, and of some similar substances sold under their descriptive chemical names, further tests for para-hydroxybenzoic acid were required by the author, as the test depending on the relative insolubility of the para-acid in chloroform is not sufficiently delicate for the detection of small quantities. Salicylic acid obtained from some samples of acetylsalicylic acid was found to be not so pure as ordinary pure salicylic acid; a second fraction of the crystals did not melt so sharply nor at the same temperature as the first fraction. The impurities one would naturally suspect are cresotic acids, para-hydroxybenzoic acid, and phenol. In one case phenol was detected, but in the other cases the impurity was in very small amount, and was not identified.

The test described by B. Fischer (*Pharm. Zeit. f. Russ.*, 1889, **28**, 378) for the detection of cresotic acids, and depending on the greater solubility of the calcium salts and on the character of the acids set free from the calcium salts, was found to work well. No cresotic acids were found in the acetylsalicylic acids nor in recent samples of salicylic acid. Though para-hydroxybenzoic acid was not found in the samples examined, a statement of the method devised may be worth recording; further, the examination of the salicylic acid led to a careful redetermination of the melting-point of salicylic acid, which was found to be distinctly higher than the figure usually given.

The Melting-Point of Salicylic Acid.

The melting-point of the acid is variously recorded: in Richter's *Organische Chemie* (1913) it is given as 155° C.; B. Fisher (*Pharm. Zeit.*, 1889 [34], **42**, 327) and Dunstan and Bloch (*Pharm. J.*, 1890 [3], **21**, 429) give the same figure—viz., 156·75° C.; in the latter case the authors purified the salicylic acid from a sample containing cresotic acids. The British Pharmacopœia states that the melting-point should be 156° to 157° C.

Salicylic acid from a number of sources was used for these experiments: (1) Two commercial specimens; (2) a specimen supplied by Professor Greenish, prepared from the hexa-hydrate of sodium salicylate, which had been recrystallised three times; (3) a specimen of salicylic acid prepared from oil of wintergreen. The acids were dried in a vacuum over sulphuric acid; they were also recrystallised from water and dried as before over sulphuric acid. The melting-points were taken with a short stem thermometer, calibrated against a standard thermometer tested at the National Physical Laboratory. The melting-point in every case was 158·5° C. both before and after crystallisation. Two very old specimens in the museum of the Pharmaceutical Society were of poor colour, and contained cresotic acids; they melted at 145°-146° C. and 151° C. respectively; after one crystallisation from water the latter

melted at 153°-154° C., but still contained cresotic acids; further purification was not proceeded with.

Three specimens of salicylic acid derived from different preparations of acetylsalicylic acid melted at 158·5° C. when recrystallised, but the residual acid extracted from the mother liquors melted at 156°-157° C. in two cases.

The addition of para-hydroxybenzoic acid to salicylic acid lowers the melting-point. The melting-point of para-hydroxybenzoic acid is usually given as 210° C., though one textbook (*loc. cit.*) mentions 213° C. Kahlbaum's pure acid melts at 213·5° C., the same melting-point being obtained after crystallisation and drying in a vacuum over sulphuric acid. If the melted acid is allowed to solidify, and the melting-point is again determined, it is found to be lower, from 210° to 211° C.; this is probably due to decomposition of the acids with the formation of a little phenol. Pure salicylic acid after melting and solidification was found to melt at the same temperature as at first.

Salicylic Acid.	Para-Hydroxybenzoic Acid.	Melting-Point.
99	1	155°–156° C.
95	5	149°–151° ,,
90	10	146°–147° ,,

On solidifying and remelting, the last two melted at about 0·3-0·5 of a degree lower. Samples of salicylic acid containing 1 per cent. of para-hydroxybenzoic acid would melt at a temperature almost within the limits required by the British Pharmacopœia.

Detection of Para-Hydroxybenzoic Acid.

The microscopic characters of the two acids are very dissimilar, particularly if crystallised on a microscopic slide from a solution in dry ether. Salicylic acid crystallises in the well-known feathery or leaf-like crystals, the para acid in small dense tufts. From a very dilute solution in commercial ether the para acid may crystallise in a feathery form, which, however, is very different from the salicylic acid; this is due to the water in the ether; using dry ether the dense tufts are obtained. Five per cent. of the para-hydroxybenzoic acid can easily be detected by microscopic examination, but it is not easy to be certain if only 1 per cent. of the impurity is present.

The formation of the basic calcium salt of salicylic acid, $(OC_6H_4COO)Ca,H_2O$, which is less soluble than the calcium salt of para-hydroxybenzoic acid, was made use of to concentrate the para acid. A small quantity of the acid to be tested was mixed with excess of calcium hydroxide and water, evaporated to dryness, and heated to 110° for an hour; after cooling, the mixture was extracted with a little water. The calcium salt of para-hydroxybenzoic acid with some salicylate dissolves. The aqueous extract was acidified and extracted with ether; the ethereal extract was filtered and evaporated to dryness. A solution of the dry substance in ether was placed on a microscopic slide and allowed to evaporate. The crystals were examined against a dark background, using a lens of half-inch focus and a total magnification of about 60 diameters.

Salicylic acid with only 1 per cent. of the para-hydroxybenzoic acid can hardly be distinguished from pure salicylic acid, though a few tufts of the para acid are to be found; but by taking advantage of the different solubilities of the calcium salts, and making a separation as described, there is no difficulty in recognising the tufts of para-hydroxybenzoic acid, which then predominate, though a few crystals of salicylic acid may still be seen.

In conclusion, I desire to thank Professor Greenish for valuable help in the preparation of the lantern slides used in illustrating this paper at the time of reading.

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Discussion.

The President asked whether the para-hydroxybenzoic acid could not be concentrated by steam distillation. He was under the impression that it was not appreciably volatile in steam, whereas the ordinary hydroxybenzoic acid was pretty freely volatile, particularly in high-pressure steam. It seemed curious that, in the case of a substance which crystallised so well, the usually published melting points should not be more nearly correct.

Mr. Davis wrote that crystallography alone is not of itself sufficient to warrant the statement that chemical bodies are pure; much debate has centred around these phenomena; physical constants are known to us, as analysts, as evidence of purity for the bulk of definite chemical bodies, but there are some, notably uric acid, which seem to defy our ideas of physical constants and upset the laws of phase rule.

It will be observed that the natural oil of wintergreen (*Gaultheria procumbens*), the synthetic oil obtained by the action of the elements of CO_2 on those of sodium phenate precipitated from solution by HCl, and that bearing the inscription "physiologically pure," obtained by the chemical process mentioned ("physiologically pure," meaning free from ortho-, meta-, and para-cresotic acids), are virtually identical in character. Each of these acids had melting-points (156°-157° C.), and each was crystallised under similar conditions of temperature and strength of solutions. It would seem salicylic acid has polymorphic forms, but all of these may be finally referred to the monoclinic system; we have under varying conditions oblique rhombic prisms, oblique rectangular prisms, and oblique rectangular base prisms, and if we separate salicylic acid rapidly from hot solutions we get tufts of acicular crystals, but if more slowly the crystals lie parallel one to another, the interstices become filled up, and monoclinic prism results. If crystallisation is effected from hot aqueous solution, the crystals are hollow, very few solid crystals being formed.

Pure natural salicylic acid has a melting-point of 156°-157° C., and this, of course, is also true of the pure synthetic variety; but if 1 per cent. of paracresotic acid be present the melting-point is appreciably lowered, out of all proportion to the quantity of impurity present. Paracresotic acid given internally, as paracresotate of sodium, is probably less poisonous than salicylic acid itself, and, indeed, on the Continent, has been largely administered with markedly good results. Orthocresotic acid is certainly poisonous, whilst metacresotic acid apparently has no pharmacological

or physiological action. Para-hydroxybenzoic acid melts at 210° C., and gives no coloration with ferric chloride.

Mr. SMITH, in reply, said that he had tried concentration by steam distillation, but had found it to be extremely slow, even with superheated steam, and the process he had described appeared to be simpler. It was important that the solvent should be pure. The photographs showed how variable might be the results obtained through the presence of traces of water. With regard to Mr. Davis's remarks, he thought it was well recognised that, in the presence of cresotic acid, salicylic acid crystallised in a felted mass, which was observable even without the aid of the microscope. He was himself surprised to find the melting-point so much higher in both cases than those which had been published. He believed that the inaccuracy of some of the published figures was due to want of care in drying the substance, and also to the use of uncalibrated thermometers. Moreover, the stem of the thermometer must be short; if the stem were too long, and if most of it were outside, it was difficult, even with a correction, to get accurate results. The melting-point of para-hydroxybenzoic acid was mentioned in some textbooks as 213° C. He thought the figure 210° C. must refer to the partially hydrated acid. It crystallised from water with one molecule of water of crystallisation. On drying *in vacuo* over sulphuric acid or in a steam oven, this water of crystallisation was lost, and then the higher melting-point was obtained. He thought that the British Pharmacopœia limit of 156° to 157° C. was lenient. Dunstan and Bloch, in obtaining their figure of 156·75° C., had worked on a sample containing cresotic acid, which possibly they did not completely remove.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Moisture and Bitter Principles in Hops. O. Winge. (*Wochensch. Brau.*, 1915, No. 45.)—The author defends the analytical scheme proposed by him and Jensen (ANALYST, 1915, **40**, 12) against some criticisms by Wiegmann (*Allgem. Brauer u. Hopfenz.*, 1915, 1315). The procedure adopted for the estimation of moisture consists in heating at 35° C. *in vacuo* for twenty-four hours. This method gives results identical with those obtained by exposure *in vacuo* over sulphuric acid at the ordinary temperature to constant weight, and it leaves the bitter principles unchanged. It is true higher numbers may be obtained for moisture by heating for longer periods at 35° C., or at higher temperatures, but such treatment is accompanied by loss of chemically combined moisture and changes in the constitution of the resins. Moreover, no sharply defined value is obtained for hygroscopic moisture, the results depending on the severity of the heating. It is necessary that the estimation of the resins be performed on a sample previously dried

without constitutional change, as, if undried specimens be taken, the extraction of the tannin interferes with the titration of the resin. For the extraction of the resin the author and Jensen have preferred to employ ethyl acetate, not because it extracts more resin than carbon tetrachloride, but because it extracts it completely in a far shorter time. Two hours' extraction with carbon tetrachloride is insufficient. The tasting tests cannot be regarded as very exact, but they show a certain simple relationship to the acidity factors of the α-, β-, and γ-resins. There seems to be no valid reason why these tests should not be made in beer-wort, which, after all, is the medium used in practice. As regards the degree of accuracy in the estimation of bitter principles, no very close concordance is to be expected, as the material is highly variable, even in the case of hops of the same origin. In the Carlsberg laboratory the more important analyses are made on hops gathered from plants of a single stock. J. F. B.

Illipé Nuts and the Sources of Borneo Tallow. (*Bull. Imp. Inst.*, 1915, **13**, 335-344.)—The seeds and kernels of several species of trees yielding Borneo tallow have been examined. These nuts, whatever their origin, are usually sold as illipé or illipi "nuts," although the true illipé nut of India is the product of *Bassia* species. The following values were given by the fats:

Fat from—	Sp. Gr. at 100°/15° C.	Melting-Point.	Acid Value.	Saponification Value.	Iodine Value.	Hehner Value.	Soluble Volatile Acids.	Unsaponifiable Matter.	Melting-Point of Fatty Acids.
		° C.					Per Cent.	Per Cent.	° C.
Large Pontianak or Sarawak nuts ...	0·8523	31 to 32	35·0	194·5	31·0	95·6	nil	0·6	53·0
Ditto	0·8535	32 to 33	32·0	194·3	31·4	94·6	nil	0·8	53·5
Isoptera borneensis	0·8563	29	8·5	190·7	31·8	94·9	0·5	1·0	52·4
Ditto, prepared by natives ...	0·8560	28 to 31	11·3	192·1	31·5	95·7	—	0·5	51·0
Palaquium oblongifolium	0·8553	38	7·0	190·4	35·9	95·3	0·2	1·0	58·0
B. latifolia (India)	0·857 to 0·862	—	31·8 to 41·8	188·3 to 199·8	57·6 to 61·5	—	0·2 to 0·9	2·0	43·2 to 46·0
B. longifolia (India)	0·856 to 0·861	—	19·7	195·3 to 202·7	54·8 to 60·0	—	2·35	1·4 to 2·2	45·0

C. A. M.

***Madia Sativa* Seed and Oil.** (*Bull. Imp. Inst.*, 1915, **13**, 344-346.)—A sample of *Madia sativa* seed from South Africa yielded 38·4 per cent. (on the dry seeds) of a yellowish-brown, semi-drying oil with the following characters: Sp. gr. at 15° C., 0·9252; solidification-point of fatty acids, 21·7° C.; acid value, 2·2; saponification value, 194·5; iodine value, 128·9; Hehner value, 95·8; soluble volatile acids, 0·1 per cent.; insoluble volatile acids, 0·7 per cent.; and unsaponifiable matter, 0·8 per cent. The residual meal was free from alkaloids, cyanogenetic glucosides, and saponin. As obtained by crushing the seed on a commercial scale, it would

contain about 7·0 per cent. of fat, and would have the following approximate composition: Moisture, 7·6; crude proteins, 28·2; fat, 7·0; starch, etc. (by difference), 27·0; fibre, 24·4; and ash, 5·8 per cent. Nutrient ratio, 1 : 1·5. Food units, 114. The percentage of proteins is higher than in sunflower or undecorticated cotton-seed cake. C. A. M.

Kaffir Corn ("Dari") from South Africa. (*Bull. Imp. Inst.*, 1915, **13**, 379.)—The following analytical results were obtained:

	White, South Africa, per Cent.	Red, South Africa, per Cent.	Mixed, South Africa, per Cent.	White Dari from Sudan, per Cent.	Red Sorghum from Zanzibar, per Cent.	Indian Dari, per Cent.
Moisture	11·93	12·00	11·73	8·45	10·0	12·5
*Crude proteins ...	9·79	10·83	10·01	13·06	11·2	9·3
Fat	3·22	3·37	3·06	3·30	2·8	2·0
Starch, etc. (by difference)	72·50	71·01	72·58	72·45	72·1	72·3
Fibre	1·27	1·28	1·14	1·03	1·8	2·2
Ash	1·29	1·51	1·48	1·71	2·1	1·7
Food units	105·0	106·5	105·2	113·3	107·0	101·0
* Containing true proteins	9·57	10·66	10·01	12·98	10·8	—

C. A. M.

Oil from "Owere" Seeds. (*Bull. Imp. Inst.*, 1915, **13**, 346-350.)—"Owere" seeds ("calabash nutmeg") from *Monodora myristica*, West Indies, yielded 2·2 per cent. of an aromatic volatile oil, and 35 per cent. of a dark reddish-brown fatty oil with the following characters: Sp. gr. at 15·5° C., 0·917; acid value, 56·7; saponification value, 180·6; iodine value, 110·6; Hehner value, 94·4; soluble volatile fatty acids, 1·0; and unsaponifiable matter, 1·6 per cent. The residual meal was free from alkaloids or cyanogenetic glucosides, but contained a large amount of fibre. It could probably only be used as manure. The oil could not be saponified readily, and yielded a soap of poor colour. C. A. M.

Turpentine Oil and Resin of *Boswellia Serrata*. (*Bull. Imp. Inst.*, 1915, **13**, 351-356.)—Oil of turpentine distilled from the crude gum-resin of *Boswellia serrata* from India was a greenish-yellow liquid with a sweet odour. It had sp. gr. at 15° C., 0·8446; $[\alpha]_D$ = + 31° 24′; ester value, 2·6; and ester value after acetylation, 36·4. On distillation it yielded a fraction of 89 per cent. between 153° and 160° C., and 11 per cent. between 160° and 180° C. It was a good solvent for resins such as colophony, dammar, sandarac, etc., but the varnishes thus prepared dried more rapidly and gave a less lustrous surface than those made with ordinary turpentine oil. Boswellia resin, prepared by heating the crude resin in a still by a gentle

fire, was a dark greenish-black brittle mass, with the following characters: Moisture, 0·9; ash, 0·4 per cent.; melting-point, 56° C.; acid value, 25·0; saponification value, 66·0; iodine value, 96·0; and sp. gr. at 20°/20° C., 1·050. It would only be suitable for varnishes of low grade or for dark-coloured sealing-wax. It yielded different products from colophony on distillation. C. A. M.

Composition of Wood Turpentine. M. Adams. (*J. Ind. and Eng. Chem.*, 1915, **7**, 957-960.)—The wood of single-leaf nut pine (*Pinus monophylla*) yielded on distillation a turpentine with the following characters: Sp. gr. at 15° C., 0·9702; $[n]_{D\ 15°}$, 1·4771; $[\alpha]_{D\ 20°}$ = + 21·15. After purification and fractional distillation at 15 mm., it was separated into three main fractions boiling respectively at 50° to 60° C., 60° to 80° C., and 80° to 135° C. The first contained α-pinene, the second β-pinene, and the third cadinene. These results showed that the wood turpentine from this species of pine was almost identical in physical properties and chemical composition with pure "gum" spirits.

Jeffrey Pine.—The wood turpentine distilled from the wood of *P. Jeffreyi* was separated by distillation at 15 mm. into the following fractions: At 25° to 30° C., 74; 30° to 35° C., 13; 35° to 65° C., 6; 65° to 125° C., 4; and residue, 3 per cent. The first three fractions when united and redistilled over sodium yielded a portion (about 90 per cent. of the original oil), distilling between 99° and 100·5° C. It had sp. gr. 0·6877 at 15° C. $[n]_{D\ 20°\ C.}$, 1·3890, and was optically inactive. The volatile oil from Jeffrey pine wood thus contains from 90 to 95 per cent. of normal heptane.

Yellow Pine (*P. ponderosa*).—The wood yielded a colourless oil with sp. gr. of 0·8626 at 15° C.; refractive index, 1·4727; and specific rotation, −13·15. It was fractionated into 8·7 per cent. at 156° to 164° C., 72·5 per cent. at 164° to 172° C., 16·4 per cent. at 172° to 180° C., and 2·4 per cent. of residue. The first fraction contained α-pinene, the second β-pinene, and the third limonene. The general results indicate that the volatile oil obtained by distilling pine wood under reduced pressure is similar to that obtained from the oleoresin of the same species of tree. C. A. M.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Carbohydrates and Enzymes of the Soy Bean. J. P. Street and E. M. Bailey. (*J. Ind. and Eng. Chem.*, 1915, **7**, 853-858.)—Calculated to a uniform moisture content of 10 per cent., the average analysis of a large number of samples of soy beans shows: Moisture, 10 per cent.; ash, 5·54 per cent.; protein (N × 6·25), 38·29 per cent.; fibre, 4·46 per cent.; nitrogen-free extract, 26·64 per cent.; and fat, 14·89 per cent.; whereas an average analysis of commercial soy bean flours shows: Moisture, 5·1 per cent.; ash, 4·5 per cent.; protein, 42·5 per cent.; fibre, 3·7 per cent.; nitrogen-free extract 24·3 per cent.; and fat, 19·9 per cent. A sample of soy bean meal was fully analysed, and was found to contain 31·08 per cent. of nitrogen-free extract and fibre. There were shown to be present in this 4·51 per cent. total sugars, 0·5 per cent. starch, 3·14 per cent. dextrin, 4·94 per cent. pentosans, 4·86 per cent. galactan (less 0·24 per cent. due to raffinose), 3·29 per cent. cellulose, 1·44 per cent. organic

acids, and 8·60 per cent. waxes, colouring matter, etc. Of these constituents only the first three—viz., the sugars, starch, and dextrin, amounting to 8·15 per cent.—may be considered objectionable in a diabetic diet. The finely ground meal was extracted successively with boiling 95 per cent. alcohol, cold water, malt extract, 1 per cent. hydrochloric acid, and 1·25 per cent. sodium hydroxide. It was concluded that raffinose was present from the behaviour of the extract with emulsin. The enzymes present include a protease of the peptoclastic type, a peroxidase, and a lipase. The presence of an active amylase has been corroborated. Negative results were obtained in testing for invertase and a protease of the peptonising type. Urease and a glucoside-splitting enzyme were not specially tested for, but were assumed to be present. H. F. E. H.

Comparative Experiments on the Pasteurisation and Biorisation of Milk. R. Burri and A. C. Thaysen. (*Schweiz. Milchzeit.*, 1915, **41**, Nos. 9, 16, 20, and 23; through *Int. Inst. Agric., Bull. Agric. Intell. and Plant Diseases*, 1915, **6**, 1249-1250.)—Five samples of fresh milk and three samples of old milk were submitted to the following processes: Pasteurisation at 65° C. for twenty minutes, at 63° C. for thirty minutes, and at 75° C. for thirty minutes; biorisation at 70°, 75°, and 80° C., and at a pressure of 2 or 3 atmospheres. Immediately after each experiment the milk was examined for peroxidase, catalase, time of clotting, reductase, number and species of bacteria, and taste. Peroxidase reactions were obtained with all the milks except one sample, which had been biorised at 80° C. With regard to catalase, the figures obtained were always higher for raw milk than for heated milk, but no essential difference could be found between the effect of biorisation at 75° C. and that of moderate pasteurisation. The coagulating power of the milk was not greatly affected by the heating. In estimating the reductase by Schardinger's methylene blue reaction (ANALYST, 1903, **28**, 32), it was found that the time required for decolorisation increased for each increase in temperature to which the milk had been subjected. However, with milk biorised at 80° C., only twenty-four minutes was required for decolorisation, whilst milk pasteurised at 70° C. took several hours. The effect of pasteurisation on the bacteriological content of the milks was generally greater than that of biorisation. The ordinary lactic bacteria (*B. guntheri*) survived the processes, as did also the majority of the micrococci and spores of certain soil bacteria. *B. coli* was found only in a few samples biorised at 70° C., whilst *B. aerogenes*, although present in large numbers in several samples of raw milk, did not develop in any of the heated samples. A cooked taste was noticed in some of the samples pasteurised at 65° and 70° C., but not in any of the samples pasteurised at 63° C. Several of the samples biorised at 80° C. had a cooked taste, but this was never noticed in those biorised at 70° and 75° C. W. P. S.

New Method of Determining the Proteolytic Strength of Germinated Grain in Technical Analysis: Acid Ratio. C. A. Nowak. (*J. Ind. and Eng. Chem.*, 1915, **7**, 858-859.)—A cold aqueous extract of ground malt (one of malt to three of water) is prepared by steeping the malt for exactly forty-five minutes. A portion of the clear filtrate is titrated with $\frac{N}{10}$ caustic soda, using phenolphthaleïn as

indicator; formaldehyde, rendered just alkaline with soda, is then added, and the extract again titrated. The increase in acidity is a measure of the amino groups present. The author expresses the opinion that, for brewing purposes, a malt having the greatest amount of amino groups is to be preferred, but only provided the original acidity has been fairly high, and the relation or ratio between the formaldehyde titration value and the natural acidity, obtained by dividing the number of c.c. of soda required for the former by the latter, should be as 1 : 1 or greater. "A good malt should be high in original acidity, and have an acid ratio of 1 : 1·1."

To obtain comparative figures as to the proteolytic strength of malts, the remainder of the filtrate is allowed to stand for a period of about sixteen hours, when a second acid ratio determination is made. H. F. E. H.

Separation of Soil Protozoa. N. Kopeloff, H. C. Lint, and D. A. Coleman. (*J. Agric. Research*, 1915, **5**, 137-139.)—For the separation of flagellates from ciliates an eight-day-old culture of soil organisms was employed, which was prepared by adding 100 grms. of clay loam soil to 1 litre of a 10 per cent. hay infusion, together with 0·5 per cent. of egg albumin. The numbers of protozoa in the stock culture solution were first counted by the authors' method (*Trans. Amer. Micros. Soc.*, 1915, **34**, 149-154), and recorded under classes of (1) flagellates, (2) small ciliates (12 to 20 μ), and (3) large ciliates (25 to 60 μ). Ten c.c. of the culture solution are placed by means of a sterile pipette on filter-paper previously sterilised with alcohol, and allowed to filter through for one minute. Three counts are made, and the filtrate incubated for five days at 22° C. to allow of the growth of any encysted forms. The filtration and incubation are then repeated, if necessary, until all the living protozoa of the desired type are filtered out. The filter-paper was used in from one to five thicknesses (S. and S. 589).

Number of Protozoa per 10 *c.c. of Filtrate.*

Number of Filter-Papers.	Flagellates.	Small Ciliates.	Large Ciliates.	Total.
Original solution	106,250	38,958	52,083	197,292
1	67,293	38,958	0	106,246
2	60,416	24,742	0	85,208
3	56,666	10,625	0	67,083
4	10,625	0	0	10,625
5	0	0	0	0

The numbers given are the average of three counts.

The fact that large ciliates are not able to pass through the filter at all agrees with the experience of Russell and Hutchinson (*J. Agric. Sci.*, 1909, **3**, 111-114, and 1913, **5**, 152-221). In the case of mixed cultures of protozoa and bacteria, 90 per cent. of the bacteria passed through five thicknesses of paper; and it is probably impossible to effect a complete separation of protozoa from bacteria by the filtration method, although this should prove useful in investigations concerned with the effect of protozoa on mixed, but not on pure, cultures of bacteria. H. F. E. H.

ORGANIC ANALYSIS.

Action of Cane-Sugar on Alkaline Copper Solutions. L. Maquenne. (*Compt. rend.*, 1915, **161**, 617-623).

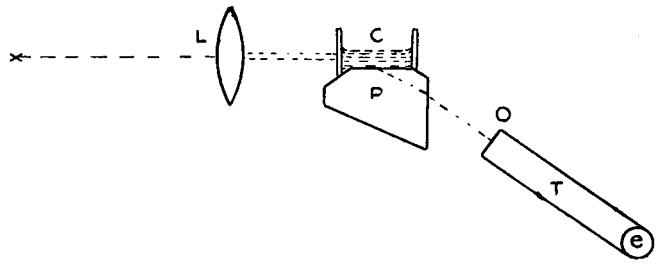
The reducing action of cane-sugar on alkaline copper solutions is infinitesimal as compared with that of invert sugar, and is modified by other influences. Thus, the cupric reducing power of cane-sugar increases rapidly with the proportion of copper present and with the time of ebullition; the difference between three minutes' and four minutes' ebullition increases the reducing power of cane-sugar by 20-25 per cent., while that of invert sugar is only increased by 3 per cent. In the present experiments the copper sulphate solution contained 40 grms. per litre, and the alkaline tartrate contained 200 grms. of Rochelle salt with 150 grms. of caustic soda per litre. Of each of these 10 c.c. were mixed and diluted to a volume between 35 and 40 c.c. (average 36·8 c.c.), allowance being made, at the rate of 0·62 c.c. per grm., for the volume of solid cane-sugar subsequently to be dissolved in the liquid. The mixture was heated rapidly to boiling (about $1\frac{1}{2}$ minutes), and maintained in gentle ebullition for exactly 3 minutes, then cooled rapidly under a stream of water. The copper was estimated by potassium iodide and thiosulphate. With increasing quantities of sugar the weight of copper reduced reached a maximum (25 mgrms. of Cu) with 4 grms. of cane-sugar; with larger quantities the cupric reduction decreased progressively, so that 10 grms. of cane-sugar reduced barely more than 2 mgrms. It is thus quite impossible to formulate any direct relation between the cupric reducing powers of cane-sugar and invert sugar. It is suggested that the decrease in cupric reduction with larger quantities of sugar is due to the formation of alkaline sucrates in solution, and that the cupric reducing action of cane-sugar does not depend on any splitting up of its molecule into the constituent monoses. The cupric reducing power of cane-sugar is decreased by the presence of invert sugar, because the more rapid reducing action of the invert sugar quickly decreases the quantity of copper in solution. In the case of mixtures of invert sugar with cane-sugar up to 8 grms. of the latter in 36·8 c.c., the cupric reduction of the mixture is less than that of the sum of each of the components separately; in presence of 10 grms. of cane-sugar the reduction is about equal to that of the components, and in presence of 12 grms. and over it becomes greater. This is owing to the influence of the sucrates, which behave as salts of copper with a feeble acid and increase the reducing power of invert sugar.

J. F. B.

Micro-reactions of Carbon Disulphide. J. Denigès. (*Bull. Soc. Chim.*, 1915, **17**, 359-360.)—The very characteristic crystalline form of the dithiotrimercuric salts, their sparing solubility, and the comparatively large quantity obtained (ten times) per unit of carbon disulphide, constitute excellent conditions for the basis of a qualitative microchemical test. For the identification of carbon disulphide, a small quantity of the substance is dissolved or suspended in about 10 c.c. of water, and treated either with an equal volume of mercuric sulphate reagent (5 grms. of mercuric oxide, 20 c.c. of sulphuric acid, and 100 c.c. of water), or with 0·3 to 0·4 grm. of mercuric chloride, or else with 2·5 c.c. of the commercial 80 per cent.

solution of mercuric nitrate, or 2 grms. of the solid nitrate and 5 or 6 drops of nitric acid. The mixture is heated in the boiling water-bath for fifteen minutes in the case of the sulphate or nitrate, or for one hour in that of the chloride. After cooling, the deposit is examined under the microscope. The nitrate forms fine hexagonal plates, the chloride forms groups of crystals like a fish-bone or fern-leaf, and the sulphate small prisms or lozenge-like plates. J. F. B.

Adulteration of Chinese Wood Oil. J. C. Brier. (*J. Ind. and Eng. Chem.*, 1915, **7**, 953-955.)—Chinese wood oil has an anomalous optical dispersion, the spectrum showing blue and green on the top, with red on the lower side; while in the case of other oils the spectrum has red on the upper side, and green and blue on the lower side. On adding other oils to Chinese wood oil, the "turning-point" of the spectrum varies within the limits of 14·5 and 17·0 per cent.; but if the exact adulterant be known, it may be estimated within ±1·25 per cent. The principle of the author's apparatus is that of the Pulfrich refractometer, and is shown in the accompanying figure. The prism, *P*, is a 90° prism, with refractive index 1·62.



T is the telescope; *C* the cell, which is so mounted that the upper surface of the prism is above the joining of the cell and prism; *L* a condensing lens; and *X* the source of light. The effect of the gradual addition of various oils to Chinese wood oil is shown in a table. In each case, at 0·5 per cent. below the "turning-point," the spectrum showed only a yellow band, while with an adulteration of 1 per cent. less than this there were two distinct bands, one green and one yellow. The temperature had a pronounced effect upon the spectrum of adulterated oils, but this factor appeared to be the same for each of the oils examined. In testing a sample for linseed oil, if the spectrum appears inverted, the oil is pure, or contains less than 8 per cent. of adulterant. An addition of 15 per cent. of pure linseed oil is then made, and if only a yellow band now appear in the spectrum the sample was undoubtedly pure. If, however, the spectrum is reversed, the sample was certainly adulterated, though not to the extent of more than 8 per cent. The depth of the colours will afford some idea of the amount of adulteration. If the green is very indistinct, it will probably not exceed 2 per cent. In order to estimate the quantity of adulterant, the amount to be added before the "turning-point" is reached is found, and this is deducted from 15·5 per cent. This is the average quantity required to reach the "turning-point" by the addition of soya bean, tallow seed, sesamé, arachis, and candle nut oils, which are stated to be the most common

adulterants of Chinese wood oil. The following results were thus obtained with commercial samples: (1) 3·75; (2) 9·00; (3) 3·5; and (4) 8·5 per cent. of added oil.

C. A. M.

Effect of Free Fatty Acids upon the Flash and Fire Points of Animal Fats and Oils. A. Lowenstein and J. J. Vollersten. (*J. Ind. and Eng. Chem.*, 1915, **7**, 850.)—The presence of free fatty acids having been observed to depress the flash and fire points of the fats and oils containing them, the authors prepared both the neutral glycerides and the total fatty acids of samples of fats showing differences in their free fatty acids.

In nearly all cases the fire and flash points of the neutral glycerides and of the total fatty acids so prepared were found to be similarly depressed. The Cleveland open fire-tester was used for determining the flash and fire tests.

H. F. E. H.

New Test for Isothiocyanates. G. Denigès. (*Bull. Soc. Chim.*, 1915, **27**, 380-381.)—The usual test for alkali isothiocyanates, the formation of a crystalline precipitate with mercuric salts, is not very delicate, being difficult to detect at concentrations below 1 per cent.; it is also not very characteristic. A better test is based on the formation of dithiotrimercuric salts, particularly the sulphate, on boiling, according to the equation

$$2CS.NM + 3HgSO_4 + 4H_2O = S_2Hg_3SO_4 + 2CO_2 + 2NH_3 + 2MHSO_4.$$

A few c.c. of the liquid containing the isothiocyanate are treated with an equal or double volume of mercuric sulphate reagent. The mixture is shaken, filtered if necessary, and the solution heated at about the boiling-point for at least one minute. A cloudiness at first develops, changing to a crystalline precipitate as heating is continued. At high dilutions it may be necessary to heat at boiling-point for four to five minutes, in which case it is best to place the tube in a boiling water-bath from the first. The reaction is sensitive to 0·25 grm. of isothiocyanic acid per litre. The crystals may be identified microscopically as prisms grouped in masses in fairly regular radial arrangement. Occasionally, especially from highly dilute solutions, the precipitate occurs as twin crystals, which may be likened to a double-headed battle-axe.

J. F. B.

Estimation of Methyl and Ethyl Alcohol in Spirit Varnishes. G. W. Knight and C. T. Lincoln. (*J. Ind. and Eng. Chem.*, 1915, **7**, 837-843.)—Spirit varnish, in addition to methyl and ethyl alcohol, may contain acetone, other ketones, and pyridine. If acetone and pyridine are absent, a modification of the Leach and Lythgoe method (*J. Amer. Chem. Soc.*, 1905, **27**, 964) is recommended, but in their presence a method based on the preparation of the iodides of the two alcohols and the determinations of their sp. gr. is employed. The authors find that methyl iodide has a sp. gr. at $\frac{15{\cdot}6^\circ\ C.}{15{\cdot}6^\circ\ C.}$ of 2·2920, and at $\frac{25^\circ\ C.}{25^\circ\ C.}$ 2·2700; while ethyl iodide

at $\frac{15{\cdot}6^\circ\text{ C.}}{15{\cdot}6^\circ\text{ C.}}$ is 1·9470, and at $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$ is 1·9300. A number of mixtures of the alcohols containing various percentages of methyl and ethyl alcohol, some without acetone and some containing up to 20 per cent. of crude acetone, were analysed, and the percentages by volume of methyl and ethyl alcohol calculated from the sp. grs. of the iodides. Riche and Bardy's method for the detection of methyl alcohol in crude alcohol (*Compt. rend.*, 1875, **80**, 1076) was employed when the percentage of methyl alcohol in total alcohol fell below 10 per cent. Details are given for the preparation of the two alcohols and their iodides in a pure state from the varnish and the following formulæ are deduced:

1. In the absence of methyl alcohol, the percentage of ethyl alcohol is equal to $\frac{3{\cdot}622\ V_1\ V_3}{V}$, where V = volume of varnish used, V_1 = volume of alcoholic distillate, and V_3 = volume of iodides obtained.

2. If the alcoholic distillate contains no ethyl alcohol, the percentage of methyl alcohol in the varnish = $\frac{3{\cdot}315\ V_1\ V_3}{V}$.

3. When both methyl and ethyl alcohol are present, the percentage of total alcohol = (0·3315 A + 0·3622 B) V_1 V_3, where A = per cent. of methyl alcohol by volume of total alcohol, and B = per cent. of ethyl alcohol by volume of total alcohol. The values of A and B are obtained by determining the sp. gr. of the mixed iodides at 15·6° C., the following formulæ being employed:

$$\text{Per cent. methyl alcohol} = \frac{3905\ (G - G_2)}{39{\cdot}05\ (G - G_2) + 51{\cdot}25\ (G_1 - G)},$$

where G = sp. gr. of mixed iodides, G_1 = sp. gr. of methyl iodide (2·292), and G_2 = sp. gr. of ethyl iodide (1·947). H. F. E. H.

Paper Fibre Analysis. M. Cline. (*Chem. Engineer*, 1915, **22**, 164-166.)—The estimation of mechanical wood-pulp in paper by colorimetric comparison or by microscopic computation does not admit of any high degree of accuracy, and the reports of different analysts, even when backed by considerable experience, may show such wide divergencies as to be useless for practical purposes of any importance. This is illustrated by specimen reports from four laboratories on samples submitted to them, and it is pointed out that a variation of 5 per cent. in the composition of a sulphite and mechanical wood-paper may involve appreciable commercial consequences. On the other hand, the chemical methods of estimation, although far more tedious, are capable of yielding perfectly concordant results, and, when carefully standardised, satisfy all the necessary requirements of accuracy. One of the most consistently satisfactory of these is the phloroglucinol absorption method devised by Cross, Bevan and Briggs (*Ver. Pap. u. Zellst. Chem., Hauptversamm.*, 1907), in which the amount of phloroglucinol absorbed from a standard solution is estimated by titration with formaldehyde. A degree of accuracy of 1 or 2 per cent. is often attained in simple mixtures of sulphite and mechanical pulps. Another process which gives satisfactory results is the estimation of the cellulose in the dry fibre of the paper by Cross and Bevan's chlorination method, calculating the results from estimations made with the pure pulps respectively. J. F. B.

INORGANIC ANALYSIS.

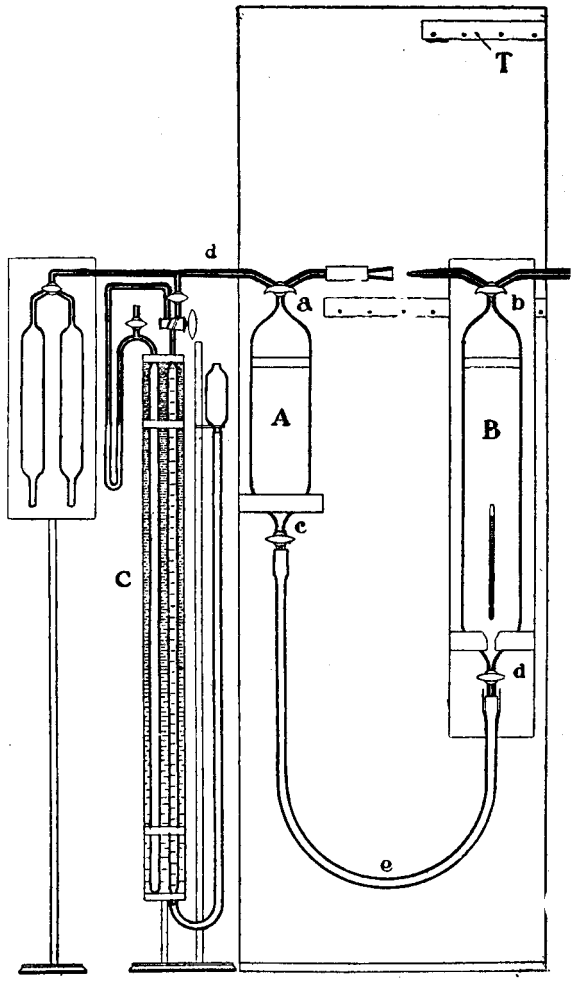
Effect of Ammonium Chloride upon Ferric and Aluminium Hydroxides during Ignition. H. W. Daudt. (*J. Ind. and Eng. Chem.*, 1915, **7**, 847.)—Hillebrand claims that a complete removal of ammonium chloride from aluminium hydroxide before ignition is unnecessary, and the author completely confirms the statement both as regards iron and aluminium. It is of advantage to have small quantities of ammonium chloride present in the wash-waters, since these precipitates tend to become colloidal when electrolytes are absent. Aluminium hydroxide can be readily filtered and washed if the faintly acid solution is boiled, precipitated with ammonia, and again boiled for a time not exceeding one minute. The solution is then immediately transferred to the filter, no attempt being made to decant the supernatant liquid. H. F. E. H.

Method and Furnace for the Determination of the Softening Temperature of Coal Ash under Fuel-Bed Conditions. A. C. Fieldner and A. L. Field. (*J. Ind. and Eng. Chem.*, 1915, **7**, 829-835.)—A special furnace is described for use in determining the softening temperature of coal ash when made into small moulded cones with 10 per cent. dextrin solution, the coal ash being previously ground sufficiently fine to pass a mesh 200 to the inch. The furnace is heated by means of a mixture of equal volumes of hydrogen and water vapour, the hydrogen being passed through water kept at a temperature of 81° C. by special regulating devices. Measurements of temperature are made through a glass window in the furnace by means of an optical pyrometer. There is no single definite melting-point, but a softening interval, and the temperature of initial deformation of the ash cone should be recorded, as well as the softening-point at which the cone either collapses to a more or less spherical lump, or the top bends over and touches the base. The average softening-point of fifty miscellaneous samples of coal ash determined in the furnace described was 1291° C., ranging from 1060° to 1596° C. Useful information as to method and amount of clinker formation of furnace coals is obtainable by the use of the apparatus, full drawings and details of which are given. H. F. E. H.

Estimation of Fluorine. W. H. Adolph. (*J. Amer. Chem. Soc.*, 1915, **37**, 2500-2515.)—Fluorine in silicate minerals may be estimated accurately by the Berzelius-Rose method, provided that the silica separated from the extracted melt is re-fused with sodium and potassium carbonates. The mineral is mixed with silica and potassium and sodium carbonates, fused, extracted with water, the silica separated by treatment with ammonium carbonate and ammoniacal zinc oxide solution, and the fluorine then precipitated with calcium chloride in the presence of sodium carbonate. The residue from the extracted melt is mixed with the separated silica, and the mixture again fused and treated as described. The precipitated calcium fluoride is extracted with 10 c.c. of 1·5 *N* acetic acid to remove calcium carbonate; this quantity of acid dissolves 0·0015 grm. of calcium fluoride, and the results obtained are corrected accordingly. Of methods which depend on the volatilisation of silicon tetrafluoride, collection of the gas in water, and sub-

sequent titration of the acidity, the best is that described by Offermann (*Zeitsch. angew. Chem.*, 1880, **3**, 615). The sulphuric acid used for decomposing the fluoride in this test should contain 98·6 per cent. of H_2SO_4. The results obtained by the method are, however, about 1 per cent. too low. Soluble fluorides can be most accurately estimated by precipitation as lead chlorofluoride (*cf.* Starck, ANALYST, 1911, **36**, 303). The colorimetric method described by Steiger (ANALYST, 1908, **33**, 139) is the most satisfactory one for detecting and estimating very small quantities of fluorine in minerals. W. P. S.

Estimation of Gases dissolved in Waters and Effluents. A. A. Swanson and G. A. Hulett. (*J. Amer. Chem. Soc.*, 1915, **37**, 2490-2500).—The method consists essentially in introducing the water into a vacuum, and, by shaking, bringing the system to an equilibrium, so that the dissolved gases are properly distributed between the gas and liquid phase. By analysing the gas phase and knowing the temperature and volumes, the amounts of gases in the two phases can be calculated. The method does not require the removal of all the dissolved gases from the water in order to determine their amount. The apparatus used consists of two glass reservoirs or bulbs (see figure) having a capacity of 1 litre and 0·5 litre respectively. The small bulb, *A*, is mounted permanently, whilst the larger bulb, *B*, is so arranged that its carriage permits of horizontal and vertical movements. The bulb *A* is connected by a capillary, *d*, with a gas analysis apparatus. The water to be examined is drawn directly into the bulb *B*, the taps are closed, and the bulb is connected with bulb *A* by means of a rubber tubing and a mercury seal. On opening the lower taps, *e* and *d*, on the two bulbs, the mercury in bulb *A* flows into the lower half of bulb *B*, and displaces an equal volume of water through the upper three-way tap *b*. This tap is then closed, and the bulb *B* is raised to the position indicated at *T*;



the mercury flows back into the bulb A, leaving the water in bulb B under reduced pressure. The tap d is now closed, the bulb B is removed from its support and shaken for two minutes, then replaced on its support, lowered to its original position, and again connected with the lower end of bulb A. The bulb B is then moved horizontally, so that it is connected with bulb A by the ground-in joint at the top; the taps a and b are placed in connection with one another, the air is exhausted from the tube between them, and the tube then filled with mercury up to the tap b. The apparatus is then ready for the transfer of the gas bulb from B to bulb A without changing its pressure, an equal volume of mercury flowing from bulb A to bulb B. The gas may be brought to any desired pressure over mercury, transferred to the gas burette, and analysed in the usual way. The temperature is read on the small thermometer fastened to the inner wall of bulb B. From the amount of gases found, the volume and temperature when in equilibrium with the water in bulb B, and the known coefficients of distribution of the gases, the total amount, x, of the gases dissolved in the water is calculated from the formula

$$x = a\left[\frac{c\,(T-t)}{T} + 1\right],$$

where a = number of c.c. of the gas removed; c = solubility coefficient of the gas at the temperature observed; t = temperature at which the gas and liquid phases wer at equilibrium; T = absolute temperature of Centigrade scale.

Should the volumes of the liquid and gas phases in the bulb not be equal, the above formula is modified as follows:

$$x = \frac{a}{b}\left[\frac{bc\,(T-t)}{T} + d\right],$$

where b = volume of the liquid phase, and d = volume of the vapour phase. The results obtained by the method agree with those found by Winkler's method.

Seyler's method (ANALYST, 1897, **22**, 312) is recommended for the estimation of free carbon dioxide in water.

The authors also described a method and apparatus for the estimation of dissolved oxygen in water. The sample of water is shaken in a glass bulb, such as the bulb B described above, with pure nitrogen until equilibrium is established. The gas phase is then passed through potassium hydroxide solution, and next over glowing copper foil, which retains the oxygen. The copper foil and copper oxide are then heated in an atmosphere of hydrogen, and the volume of hydrogen required to reduce the copper oxide is measured; the volume of the oxygen is one-half the volume of the hydrogen required. W. P. S.

Tables for the Determination of Gems and Precious or Ornamental Stones without Injury to the Specimen. A. J. Moses. (*School of Mines Quarterly*, 1915, **36**, 199-232.)—The classification of the gem minerals is arranged in ten tables, according to colour. All the tests included in these tables, except the hardness (which is recorded but made subordinate), can be performed without injury to cut and polished stones. A supplementary table is added for confirmatory tests when fragments are available for recording the effects of heat and

acids. All the tests are described in detail in the text thus: A. Tests of supplementary tables and crystallographic tests: 1, Effects of moderate heat; 2, effect of blowpipe heat; 3, effect of concentrated hydrochloric acid; 4, effect of dilute hydrofluoric acid; 5, bead tests; 6, recognition of crystal symmetry and system; 7, determination of cleavage; 8, identification of natural crystals by angles and symmetry; 9, determination of specific gravity; 10, hardness. B. Tests of the principal tables: 11, Preliminary tests with the microscope; 12, determining single or double refraction, determining index of refraction for the D line of the spectrum; 13, index of refraction by refractometer; 14, index of refraction by the microscope; 15, pleochroism of a cut stone with the microscope; 16, pleochroism in cut stone with the dichroscope. C. Special optical tests of "birefringence," uniaxial or biaxial, positive or negative optical character: 17, Birefringence with refractometer; 18, uniaxial or biaxial with microscope, interference figures; 19, optical character; 20, determination of the axial angle; 21, Differentiation of synthetic and natural corundum; 22, detecting doublets. The complete scheme is the basis of a course of instruction in gem minerals at the Columbia University. J. F. B.

Action of Magnesium on the Sulphides of Tin, Antimony, and Arsenic. **C. Pertusi.** (*Ann. Chim. anal.*, 1915, **20**, 229-233.)—When stannous sulphide is treated in presence of water with magnesium powder, sulphuretted hydrogen is evolved, the liquid becomes alkaline and contains magnesium polysulphides, while the residue contains metallic tin. If the stannous sulphide be treated with magnesium in presence of hydrochloric acid, and the magnesium be added in quantity 4-5 times that of the stannous sulphide, the reaction becomes quantitative after a sufficient time, and the whole of the tin is found in the solution at the ordinary temperature. Stannic sulphide, when treated with magnesium in presence of water, is converted partly into stannous sulphide and partly into metallic tin; the relative proportions of these products vary according to the quantity of magnesium and its fineness. Both the sulphides of arsenic react with magnesium in the cold, but the temperature rises and the reaction becomes complicated; some arseniuretted hydrogen is evolved, and the magnesium polysulphides combine with the arsenic sulphide. Possibly magnesium arsenide is among the products, since a large evolution of arseniuretted hydrogen is observed on treating the residue with acid. Antimony sulphide behaves in a similar manner, but the solubility of the sulphide in the magnesium polysulphides is less pronounced. The presence of tin sulphide in conjunction with arsenic or antimony sulphides facilitates the production of arseniuretted or antimoniuretted hydrogen, possibly by combination with the metallic tin. When all three metals are present together, the precipitate of mixed sulphides is divided into three parts. In the first portion the test for tin is made by treating with magnesium powder, shaking and warming until the yellow colour changes to brown. The liquid is filtered, the residue on the filter treated with hydrochloric acid, and tested for tin by the addition of mercuric chloride to the clear filtrate. The second portion is treated with magnesium powder and 4-5 c.c. of methyl alcohol; it is shaken for a few minutes, warmed slightly, and filtered through a dry filter; the filtrate is

allowed to drop into concentrated hydrochloric acid, when, if arsenic be present, it is precipitated as sulphide, while the antimony remains in solution. This test readily shows small quantities of arsenic (down to 1 mgrm.) in presence of large proportions of tin or antimony. The third portion is tested for antimony by the reaction of Gastaldi and Pertusi; the precipitate is dissolved in concentrated hydrochloric acid in the form of trichloride, the solution is filtered and tested with a drop of mercuric chloride solution, and then an excess of potassium hydroxide; a black precipitate or cloudiness indicates the presence of antimony. J. F. B.

Estimation of Nitrates in Soil. R. S. Potter and R. S. Snyder. (*J. Ind. and Eng. Chem.*, 1915, **7**, 863-864.)—Lipman and Sharp (*Univ. Cal. Pub. Agr. Sci.*, 1912, **1**, 21) have shown that the use of alum, alumina cream, and bone-black, for coagulating the clay and organic matter when preparing the soil extract to be used for the estimation of nitrates, causes a decided loss in the amount of nitrates found. They recommend the use of quicklime for this purpose, and state that the use of 2 grms. of calcium oxide to 100 grms. of soil gave the whole of the nitrate nitrogen in a soil of known nitrate content. The authors show that with soils low in nitrates the use of calcium carbonate is to be preferred to calcium oxide, and when the colorimetric phenoldisulphonic acid method is used the carbonate is always better. Carbonate in all cases yields as clear and as nearly colourless a solution as the oxide. In every type of soil examined calcium oxide gave lower results than the carbonate. H. F. E. H.

Detection and Estimation of Very Small Amounts of Phosphoric Acid, especially in Water. P. Medinger. (*Chem. Zeit.*, 1915, **39**, 781-782.)—The reagent used in the method is prepared as follows: Forty grms. of ammonium molybdate are dissolved in 100 c.c. of water, and a saturated strychnine nitrate solution is added until the precipitate which at first forms no longer dissolves; about 80 c.c. of the strychnine nitrate solution are required. The solution is then poured into an equal volume (about 180 c.c.) of nitric acid (sp. gr. 1·4), the mixture is allowed to stand overnight, and filtered. For the detection of phosphoric acid in water, 20 drops of the reagent are placed in a test-tube, 10 c.c. of the water are added, and the contents of the tube are shaken. If as little as 0·25 mgrm. of phosphoric acid (P_2O_5) is present per litre of the water, a turbidity develops within twenty seconds; with 2·5 mgrms. of phosphoric acid per litre the turbidity appears at once, and a precipitate forms in about twenty seconds. The above prescribed ratio of reagent to solution under examination should be maintained if smaller quantities of water are used for the test. Although the usual constituents of drinking waters (silica, lime, magnesia, iron, and organic substances) do not interfere with the test, they may cause a precipitate to form after some length of time; any turbidity which develops after the lapse of twenty seconds should not, therefore, be taken as indicating the presence of phosphoric acid. The sensitiveness of the reagent decreases slightly after a few days, but may be restored by the addition of a few drops of strychnine nitrate solution. The test may also be applied to the detection

of phosphoric acid in wine, etc., and the quantity of phosphoric acid present may be estimated approximately by comparison with standards prepared under similar conditions. W. P. S.

Estimation of Selenium in Sulphur. W. Smith. (*J. Ind. and Eng. Chem.*, 1915, **7**, 849-850.)—When the bromides of sulphur and selenium are shaken with an excess of cold water, decomposition takes place as follows:

$$2S_2Br_2 + 3H_2O = H_2SO_3 + 3S + 4HBr.$$
$$Se\,Br_4 + 3H_2O = H_2SeO_3 + 4HBr.$$

The decomposition of the selenium bromide proceeds rapidly compared with that of the sulphur bromide. When the acids of selenium are heated with excess of hydriodic acid, they are reduced to selenium, thus:

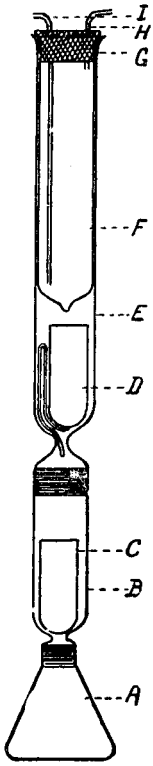
$$H_2SeO_4 + 6HI = 4H_2O + 3I_2 + Se.$$
$$H_2SeO_3 + 4HI = 3H_2O + 2I_2 + Se.$$

About 50 grms. of the sulphur in which it is desired to estimate selenium are finely powdered, and treated with rather more than 50 c.c. of bromine. After standing for about fifteen minutes, the whole is transferred to a 100 c.c. separating funnel and shaken vigorously with 40 c.c. of bromine water for one minute. The undecomposed sulphur bromide is separated from the aqueous solution containing the selenious and selenic acids, which is poured through a wetted filter-paper. The sulphur bromide is extracted four times with about 2 c.c. of bromine and 40 c.c. of bromine water. If insufficient bromine be added, sulphur will separate during the extraction. The last extract should be free from selenium, or the extraction of the sulphur bromide must be continued. The combined extracts, which must contain an excess of bromine, are boiled until clear, any remaining free bromine being removed by potassium bisulphite or sulphite. At this stage selenium in the red form may begin to separate; the whole is then diluted to about 250 c.c., and boiled with 15 c.c. of hydrochloric acid and about 5 grms. of potassium iodide, thus completing the precipitation of the selenium and converting the red into the black variety. The free iodine is removed with potassium bisulphite, and, after boiling for twenty minutes, the selenium is filtered through a tared Gooch crucible, washed with hot water, and dried at 100° C.

Japanese samples of commercial sulphur were found to contain from 0·3 to 0·8 per cent. of arsenic, and from 0·04 to 0·15 per cent. of selenium. Tellurium, if present, will be estimated as selenium by the above method, and may be separated from the selenium by the method of Browning and Flint (ANALYST, 1909, **34**, 509).

H. F. E. H.

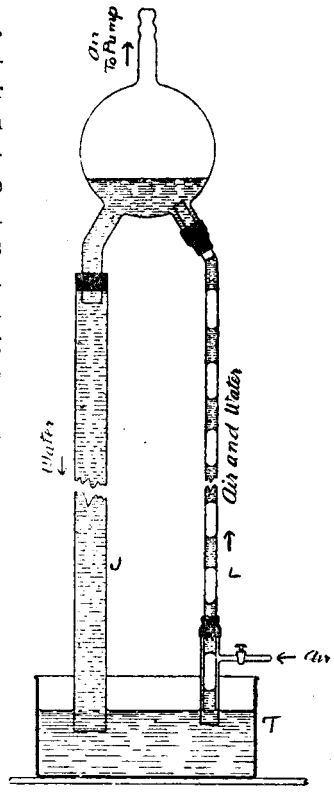
APPARATUS, ETC.



Apparatus for Fat Extraction. I. Selecter. (*J. Ind. and Eng. Chem.*, 1915, **7**, 871.)—The condensing section *E* is 18 inches long and 1·5 inches in diameter, flanged slightly at the top, and drawn out at the bottom into a ground-glass end to fit the top of section *B*. Into *E* is placed a Soxhlet extraction-tube (*D*), fitted with a siphon-tube at the side. Above is the condenser proper (*F*), which is $1\frac{1}{4}$ inches in diameter, and hangs with a flange from the top of *E*. It is fitted with a rubber stopper (*G*), having two holes to admit of a cooling water-supply and exit. *B* contains the thimble *C*, 5 inches long and 1 inch in diameter. The reservoir *A* consists of a 75 c.c. Erlenmeyer flask ground to fit *B*. The solvent liquid passes in a state of vapour through *B*, and condenses and falls into *D*, until in siphoning over it floods *C* and effects extraction, and when this is complete, *C* is removed, replaced by a glass capsule of similar size, and the solvent collected. Figures are cited showing that higher values are obtained for ten different materials than those yielded by the Soxhlet or "straight flow-through" methods. H. F. E. H.

Determination of the Concentration of Hydroxyl Ions. F. Francis, F. H. Geake, and J. W. Roche. (*J. Chem. Soc.*, 1915, **107**, 1651-1673.)—The method for the determination of hydroxyl ion concentration based on measurements of the rate of decomposition of nitrosotriacetonamine (*J. Chem. Soc.*, 1912, **101**, 2358; 1913, **103**, 1722) has been further developed. By measuring the pressure instead of the volume of nitrogen evolved, results for the unimolecular constant were obtained of a much higher degree of accuracy than previously, without serious diminution of the rapidity of the experiments. In a few experiments on the hydrolysis of sodium carbonate the new method gave data in good agreement with those deduced from conductivity and electro-motive force measurements. The catalysis of other nitrosoamines has been studied in the hope that some light would be thrown on the nature of the reaction, but no definite conclusions could be drawn. This part of the investigation, however, led to the adoption of nitrosovinyldiacetonamine and nitrosoisobutyldiacetonamine to bridge that region of ionic concentration which, owing to the "drift" in the constants, cannot be measured through the agency of nitrosotriacetonamine. In small concentrations of the catalytic agent a general similarity was found in the catalyses of all the nitrosoamines examined, but in concentrated solutions this was not the case, and, further, a well-marked divergence was observed in the behaviour of potassium and sodium hydroxides. Numerous results have been accumulated on the action of neutral salts on the course of the catalysis. A modified form of apparatus is described suitable for measurements either by the old method or by the new method of pressure determinations. J. F. B.

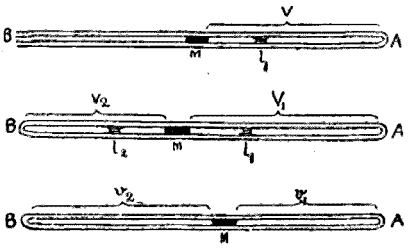
Laboratory Circulating Pump. J. S. Morgan. (*J. Chem. Soc.*, 1915, **107**, 1710-1711.)—A simple apparatus is described for maintaining a circulation of water from a thermostat, through the jacket of any portion of an apparatus which must be kept at constant temperature, and back again to the thermostat. In the accompanying figure, *T* represents the thermostat, and *J* the jacket surrounding the portion of the apparatus under observation. To the top of *J* is fixed a bulb with three inlets, as shown. One of these inlets is connected to *J*, one to the water-pump, and the third to a long tube, *L*, which just dips into the thermostat. Over the end of *L* a somewhat wider tube, fitted with a side-branch, is fixed with a rubber connection. The side-branch, controlled by a stopcock, serves as a means of adjustment; by completely closing the stopcock, water only is raised by the pump. On opening the cock a mixture of air and water is raised, which on reaching the bulb separates into water, which returns to the thermostat by way of the jacket *J*, and air which passes away through the pump. By increasing the number of intake-tubes, very large jackets can be kept supplied with sufficient water so that the temperature gradient becomes almost negligible. J. F. B.



Method of Mechanical Soil Analysis. O. Swen. (*Int. Mitt. für Bodenkunde*, 1915, **5**, 257-311; through *Int. Inst. Agric., Bull. Agric. Intell. and Plant Diseases*, 1915, **6**, 1307.)—The ultimate object of mechanical soil analysis is the construction of a curve with abscissæ representing values having a mathematical relation to the diameter of the particles, and ordinates representing values from which the weight or number of the corresponding particles may be calculated. The construction of such a curve entails a large amount of work, and the author has endeavoured to obtain an idea of the distribution of the components, not by the isolation of the various groups, but by studying a particular character in direct relation to the size (with reference to the occurrence) of the particles. This character is the rapidity of settling of the soil particles in water. The soil sample being uniformly distributed throughout the water, the weight, *P*, of the particles sinking to the bottom is determined as a function of the time, *t*, and the curve so obtained is characteristic for each sample. The apparatus consists principally of a cylinder $11\frac{3}{4}$ inches high, filled with water. About 2 mm. above the bottom, a copper plate of about the same diameter as the cylinder is suspended by thin silver wires to one arm of an accurate compensating balance. To the other arm is attached a compensating weight, which can be increased or decreased automatically. A sample of soil is poured into the cylinder; the soil particles fall through the water and settle on the plate. As soon as the

sedimentation has begun the plate falls; shortly after it rises again, owing to the automatic increase of the compensating weight on the other arm. This process is repeated until all the soil particles are precipitated; the increase in the compensating weight represents the weight of the sample of soil. Synchronously with this operation, the time required by the soil to sink is determined by a chronograph. Thus, the speed of the sedimentation may be recorded in the form of curves; each type of soil has some special characteristic. J. F. B.

Comparative Method for Determining Vapour Densities. P. Blackman. (*J. Chem. Soc.*, 1915, **107**, 1500-1503).—A simple method for the determination of vapour densities by comparison with a liquid of known vapour density is described. A piece of ordinary glass tubing is drawn out to a straight capillary, about 50 cm. long, to act as a filler. This must be sufficiently fine to pass inside a straight piece of capillary tubing 100 cm. long, and not too wide in bore. One end, *B*, of this tube is sealed, and with the tube in a vertical position, sealed end downwards, a small bead of mercury, *M*, is placed by means of the filler about halfway down the tube. Similarly, a short thread (less than 10 mm.) of the liquid to be tested is placed between the mercury and the open end *A* of the tube, well away from *A*, which is then sealed up. The end *B* is next opened, and when the end *A* has cooled the tube is placed horizontally, and the length *V* of the air-space between *A* and *M* is measured, also the length l_1 of the thread of liquid. A similar short thread of a liquid, the vapour density of which is known (d_2), is next inserted through the end *B*, which is then resealed. After cooling, the tube is placed horizontally, and the lengths V_1 of the air thread between *A* and *M*, V_2 of the air thread between *B* and *M*, and l_2 of the second liquid, are measured. The sp. gr. s_1 and s_2 of the two liquids must be determined, also the temperature of the room, t_1, and the atmospheric pressure, *p*. The tube is next heated in a horizontal position to a temperature sufficient to volatilise both liquids, and when the bead of mercury has become stable, the lengths v_1 and v_2 of the vapour threads on either side of it are measured. The vapour density (d_1) can then be calculated by a complex formula, which may be simplified down to $\frac{s_1 l_1}{d_1 v_1} = \frac{s_2 l_2}{d_2 v_2}$, with an error of less than 1 per cent., suitable for all ordinary purposes, and reducing the number of measurements required. J. F. B.



Direct-Reading Viscosimeter. R. F. MacMichael. (*J. Ind. and Eng. Chem.*, 1915, **7**, 961-963.)—In this apparatus the oil is placed in a revolving cup within which is suspended a disc by a torsion wire about 10 inches long, which runs through the stem of a plunger and is fastened near the bottom. The cup has an oil jacket, within which is an electric heating coil, so that the temperature may be kept constant throughout

the test. At the top of the plunger is a graduated dial, secured to the stem by means of a friction disc, so that the zero mark may be adjusted. About 100 c.c. of oil are placed in the cup, which is then covered and the thermometer inserted. The liquid is heated to the desired temperature, and the excess above the level is removed by means of a pipette. Within a few seconds after starting the motor the dial will be steady, and the reading is taken in degrees of angular deflection (300° to the circle), and recorded as °M. Since water at 20° C. has $\frac{1}{100}$ of the absolute unit of viscosity, water at this temperature would read 10° M. By the use of lighter or heavier torsion wires readings for water of 100° M. and 1° M. are obtained. Calibration of the viscosimeter is best done by means of a standard solution of sugar syrup. Colloidal solutions may be tested with this instrument, and the readings are not affected by small particles of suspended foreign matter. C. A. M.

REVIEW.

A Manual of Oils, Resins, and Paints. For Students and Practical Men. Vol. I.: Analysis and Valuation. By Harry Ingle, D.Sc., Ph.D., F.I.C. With Diagrams by the Author and J. A. L. Sutcliffe, A.I.C. London: Charles Griffin and Co., Ltd. 1915. Pp. 129. Price 3s. 6d. net.

The author of this book has attempted within a comparatively few pages to deal with even a wider scope of subject-matter than the title might suggest to the reader's mind.

The work commences with a chapter on the chemistry of oils, gums, etc., followed by chapters on physical and chemical tests and classification of oils (mineral, essential, and fatty). The reader is then led to the consideration and examination of an immense number of products which are required in such industries as the manufacture of soap, candles, lubricants, waxes, varnishes, paints, turkey-red oils, turpentine and turpentine substitutes, edible oils, coal-tar products, linoleum, etc.

In view of all these subjects, it is necessary to take into account the statement made in the preface that the work is largely based on a course of lectures at Leeds University. To students attending such or similar lectures—in which the necessary amplification is given by the lecturer—the book should prove of value, but to the general analyst the descriptions, etc., are mostly too short, unless supplemented by reference to other works. At the same time, the book provides a very useful scheme for the examination of the various technical products it deals with, without the addition of a long list of limitations and contradictions, which in many larger works only perplex and hinder the student, who is probably not able to gauge them at their proper worth. While fully admitting the value of the book as regards the examination of technical materials, there is practically no guidance whatever given to the general analyst as to the interpretation of most of the tests carried out.

The author is a little inconsistent in the space he has allotted to his various subjects. For example, seven pages are justly devoted to soap, which is well dealt with, though not sufficiently to include some of the modern detergent mixtures; while waxes are dismissed in two pages, and margarine in three lines, yet nearly four pages of the very limited space are devoted to the once valuable, but now superseded, method of Hübl and its theoretical basis.

The book concludes with a useful set of tables of constants of various oils and fats, but, unfortunately, in some cases the limits given are so wide as to be little guide to those not familiar with typical figures. For instance, the iodine value of lard, given in the tables as from 46 to 70, and on p. 39 as from 67 to 88, is not only lamentably inconsistent, but would rather mystify a student who was called upon to examine a sample of lard.

The printing of the book is excellent, the diagrams are clear, and it is evident that the proofs have been carefully corrected. E. RICHARDS BOLTON.

SUGGESTED NOTICE ON RESERVED OCCUPATIONS.

THE Royal Society has brought to the notice of the Society of Public Analysts the scheduling by the Board of Trade of the following reserved occupations:

Chemists.—Analytical, consulting, and research chemists (not to be accepted for immediate enlistment or called up for service with the Colours without the consent of the Royal Society).

Chemical Laboratories.—Head laboratory attendants.

A recent official announcement states that a mark is placed on the Army Register against the name of a man actually engaged in a reserved occupation. In the event, however, of any analytical, consulting, or research chemist being accepted for immediate enlistment or called up for service with the Colours, the chemist or his employer should at once point out to the recruiting officer that he belongs to a reserved occupation, and that the consent of the Royal Society is necessary. If there is reason to doubt whether the man is entitled to have a mark placed against his name in the Army Register, the recruiting officer may take steps to have the matter investigated by the Royal Society.