MAY, 1917. Vol. XLII., No. 494.

THE ANALYST.

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

An ordinary meeting of the Society was held on Wednesday evening, April 4, 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.

A certificate of proposal for election to membership in favour of Captain Norman Mederson Comber, B.Sc. (Lond.), A.R.C.Sc., No. 2 Training Reserve Battalion, Rugeley Camp, Staffs, Assistant Lecturer in Agricultural Chemistry in the University of Leeds, was read for the first time.

Mr. H. C. S. de Whalley was elected a member of the Society.

The following papers were read: "On the Natural Occurrence in Certain Fish-Liver Oils of High Percentages of Hydrocarbons," by A. Chaston Chapman, F.I.C.; "Note on the Inflammability of Petroleum Spirit at Low Temperatures," by J. H. Coste, F.I.C.; and "Determination of Volatile Thinners in Oil Varnishes," by Armand de Waele and Frederick Smith, A.I.C.

* * * * *

ON THE NATURAL OCCURRENCE IN CERTAIN FISH-LIVER OILS OF HIGH PERCENTAGES OF HYDROCARBONS.

By A. CHASTON CHAPMAN, F.I.C.

(*Read at the Meeting, April* 4, 1917.)

In September, 1915, a sample of oil was submitted to me with the request that I would examine it and state if it consisted of genuine cod-liver oil. The oil was of a pale yellow colour and had a pronounced odour of fish oil. In the course of its examination the following results were obtained:

Sp. gr. (15°/15°C.)	0·8666°	
Saponification value	22·5	
Iodine value (Wijs)	358	
Unsaponifiable matter	89·1	per cent.
Iodine value of unsaponifiable matter ...	376·2	
Free fatty acid (as oleic acid)... ...	0·42	per cent.
Bromine precipitate insoluble in ether ...	76·5	per cent.

I reported that it consisted of approximately 89 parts of some "unsaturated hydrocarbon oil" with approximately 11 parts of some fish oil. Had my examination been restricted to a determination of the specific gravity of the sample and to an estimation of the percentage of unsaponifiable matter present, it might have been reasonable to assume that the oil consisted of a mixture of mineral oil and fish oil; and I subsequently learned that, before it was submitted to me, this verdict had, in fact, been passed upon it. A consideration of the iodine value and the percentage of bromine precipitate insoluble in ether appeared, however, to exclude this explanation entirely.

The results, in fact, perplexed me very greatly, for I was not aware of any hydrocarbon or other unsaponifiable substance possessing the properties exhibited by the unsaponifiable matter present in this oil. It seemed very probable to me, therefore, that this was not an adulterated but an abnormal specimen of oil, and I decided for my own satisfaction to submit it to a systematic investigation.

A few weeks after the commencement of my investigation, I received a copy of a report which greatly stimulated my interest in the matter. The vendors of the oil in Lisbon repudiated the suggestion that it was adulterated, and submitted a sample to Dr. Hugo Mastbaum of that city, who obtained results similar to mine, and who expressed the same opinion.

As the vendors were still not satisfied, they submitted portions of the actual livers to Dr. Mastbaum, who again obtained very similar results with the expressed oil. Still not satisfied, the merchants in question invited Dr. Mastbaum to witness the opening of several fish and to take with him portions of the livers for examination. The two species of fish, which were opened in Dr. Mastbaum's presence, appear to be known in Portugal as "Barroso" and "Carocho" respectively. According to Mastbaum, these were about 1 metre in length, were quite fresh, and the livers were "smooth and oily, and when pricked with a knife, considerable quantities of oil immediately separated, the bulk of the liver substance being transformed in the course of a few hours into an oily liquid."

In a subsequent communication (*Chem. Zeit.*, 1915, **39,** 139, 889) the following results were given by Mastbaum for these two samples of oil:

	"Barroso."	"Carocho."
Sp. gr. (15°/15° C.)	0·8637°	0·8711°
Butyro-refractometer at 25° C. ...	102	93
Polarisation in 200 mm. tube ...	-0·3	-2·33
Solidification-point	Still liquid at -7° C.	Becomes turbid at -7° C.
Saponification value	15·4	36·7
Free acids (calculated as oleic acid)	0·097 per cent.	0·165 per cent.

As I was unaware that Dr. Mastbaum had published this note, I wrote to him pointing out that I had completed the first part of an investigation of the oil, and asking him to give me any information he could in reference to its origin. He replied informing me that the oil in question was obtained from the two species of fish above referred to, and added the information that, according to a standard Portuguese dictionary, the scientific descriptions of the above fish are *Centrophorus* *granulosus* and *Scymnus lichia* respectively. He also informed me that these fish are caught in deep water off the Moroccan coast, and that they have only come into the Portuguese market since the employment of steam trawling in those fishing-grounds. He suggests that it is owing to this fact that the existence of fish-liver oils containing so large a proportion of unsaponifiable matter has hitherto escaped observation.

Into the details of the investigation of this sample of oil it is unnecessary for me to enter, since a full account of the work has recently been published in the Journal of the Chemical Society (*J. Chem. Soc.*, 1917, **111,** 56). It will suffice if I point out that the greater part of the oil was found to consist of an unsaturated hydrocarbon having the formula $C_{30}H_{50}$, and containing six ethenoid linkings, which, of course, accounts for the very high iodine value of the original oil.

Among the other compounds which I have prepared is a dodecabromide having the formula $C_{30}H_{50}Br_{12}$, which is insoluble in ether, and which is consequently obtained by the process usually adopted for the preparation of ether-insoluble brominated glycerides.

The hydrocarbon does not appear to be identical with any known hydrocarbon, and I have therefore proposed for it the name "spinacene," since both *Centrophorus granulosis* and *Scymnus lichia* belong to the *Spinacidæ* or *Squalidæ*—a family of the *Sclachoidei*, or sharks. It is optically inactive and does not solidify when cooled to $-20°$ C. Its specific gravity at 15°/15° C. $=0{\cdot}8641$, and at 20°/20° C. $=0{\cdot}8616$.

The following are the results of determinations of its index of refraction at 20°:

$n\text{H}\alpha = 1{\cdot}4932$
$n\text{D} = 1{\cdot}4967$
$n\text{H}\beta = 1{\cdot}5054$
$n\text{H}\gamma = 1{\cdot}5130$

At 150° C. its index of refraction for the D-line is 1·4987. Its specific refraction calculated by the $\dfrac{n^2-1}{(n^2+2)d}$ expression, is 0·3394, and the molecular refraction 139·1.

Taking Conrady's average numbers for the atomic specific refractions, (D-line) $C_{30}H_{50}$ with six ethenoid linkings requires 137·7.

Employing the n^2 formula, the specific dispersive power of spinacene, $r\gamma - r\alpha$ is 0·0114, and its molecular dispersion $(r\gamma - r\alpha)$M, 4·67. Taking Eisenlohr's numbers for the atomic dispersions for the α- and the γ-hydrogen lines, the calculated number is 4·33. It will be seen, therefore, that the molecular dispersion, like the molecular refraction, is high. In this connection, it is worthy of note that both the molecular refraction and the molecular dispersion of the saturated hydrocarbon obtained from spinacene agree well with the calculated numbers.

Viscosity (Time of Efflux).—Fifty c.c. of spinacene required 78 seconds to flow through the aperture of a Redwood viscosimeter at 21° C., as compared with an average of 370 seconds for rape oil.

Absorption of Oxygen.—1·662 grms. of spinacene were exposed in a flat-bottomed glass dish to an atmosphere of oxygen at the ordinary temperature. At the end of two months the hydrocarbon had absorbed 0·397 grm. of oxygen, and had become so viscous that it would not flow. Thin films of the hydrocarbon when exposed to the air formed a hard skin similar to that given by linseed oil.

Whether regarded from the analytical or from the physiological point of view, the existence of fish-liver oils containing nearly 90 per cent. of an unsaturated hydrocarbon as a normal constituent is a matter of considerable interest and importance.

At first it appeared to be just possible, notwithstanding Mastbaum's results, that the fish from which the oil was obtained were in some way or other abnormal. The fact that samples of oil having approximately the same composition were derived from fish which had been caught during periods extending over several weeks, and that the consignment represented by the sample submitted to me amounted to nearly 5,000 litres, appeared, however, to negative any suggestion of abnormality. A paper by M. Tsujimoto (*J. Ind. Eng. Chem.*, 1916, **8,** 889), which I have only quite recently seen, seems finally to settle this point, since he has obtained from the livers of certain Japanese sharks a hydrocarbon to which he has given the name "squalene," which resembles spinacene very closely, and may prove to be identical with it.

The presence of hydrocarbons in fatty oils is probably of much more frequent occurrence than has hitherto been supposed, and there can be little doubt that the unsaponifiable matters other than cholesterol, phytosterol, and similar alcohols, often consist mainly of these substances. It is well known that fish-liver oils frequently contain somewhat high percentages of unsaponifiable matters, and this would appear to be particularly the case with shark-liver oil, which, according to Lewkowitsch, may contain over 20 per cent. of such substances stated to consist chiefly of cholesterol.

In view of the results recorded in this paper, it is of considerable interest to note that Allen ("Commercial Organic Analysis," vol. ii., part i., p. 201) gives the following results for four samples of oil which he refers to as "presumably adulterated shark oil":

	A.	B.	C.	African Fish Oil.
Sp. gr. at 15·5° C.	0·8746	0·8692	0·8661	0·8672
Percentage of KOH required ...	—	4·50	5·50	—
Ether-residue	69·9	80·8	83·5	82·8

Allen says: "The ether-residue was generally of a bright yellow colour like the original oil, remained quite clear on cooling, and volatilised somewhat readily. A further examination was made of the ether-residue from sample B, which was free from nitrogen and nearly free from oxygen. It gave when heated an unmistakable odour of pine resin, and appeared to be a mixture of light rosin oil with shale or petroleum lubricating oil. With concentrated sulphuric acid, B gave a reddish-brown coloration, becoming darker on stirring."

Allen also says: "Owing to frequent adulteration, the physical and chemical characters of shark oil have been misstated by many authorities. Thus it is commonly alleged to be of very low specific gravity, a character in all probability really due to the presence of a large proportion of mineral oil or similar adulterant, which addition caused the saponified sample to yield large ether-residue. Whether or not these oils of low specific gravity were uniformly adulterated is no longer of much practical interest, as oil of such character is not now to be met with."

There can now be very little doubt that the samples examined by Allen were not, as he suspected, adulterated oils, but were samples of genuine oil obtained from certain of the *Squalidæ* or *Spinacidæ*, and consisting largely of spinacene or some similar hydrocarbon.

In 1906, Tsujimoto published in the *Journal of Chemical Industry* of Tokyo an account of a sample of oil obtained from the liver of a Japanese shark containing 56·1 per cent. of unsaponifiable matters consisting mainly of an unsaturated hydrocarbon, to which at that time he assigned the formula $C_{10}H_{18}$. In his recently-published paper, to which I have referred above, he deals with the oil obtained from the livers of two species of Japanese shark which contained from 70 to 90 per cent. of an unsaturated hydrocarbon.

Inasmuch as the existence of shark-liver oils containing such high proportions of unsaponifiable matter is now thoroughly well established, it is clear that the standards given in many textbooks will need to be very considerably revised, and that the analyst will have to proceed with caution when asked to pronounce an opinion as to the genuineness or otherwise of a sample of such oil.

Thus, Lewkowitsch ("Chemical Technology and Analysis of Oils, Fats, and Waxes," vol. ii., table facing p. 370) gives for Arctic and Japan Shark Oils numbers for the specific gravity at 15°/15° C. ranging from 0·9105 to 0·9177, whilst Allen records numbers ranging from 0·9185 to 0·9285. On the other hand, shark-liver oils consisting largely of hydrocarbon such as those referred to in this paper have a specific gravity at 15°/15° C. of 0·86 to 0·88, and it is not improbable that genuine oils having intermediate specific gravities may occur.

For the iodine value, numbers are given by Lewkowitsch varying from 137 to 162, whilst Hunt (*J. Soc. Chem. Ind.*, 1902, **21**, 455) gives a mean of 98·9. The hydrocarbon-containing oil, on the other hand, gives numbers in the neighbourhood of 360.

Again, whilst ordinary shark-liver oil gives about 20 to 25 per cent. of a bromine compound insoluble in ether, the hydrocarbon-containing oil yields as much as 76 per cent.

If, as the result of further experience, it should be found that all shark-liver oils are capable of being divided more or less sharply into two classes—namely, those which consist mainly of glycerides and those which consist mainly of unsaturated hydrocarbons—the position of the analyst will be tolerably clear; but if, as seems more probable, there is a more or less regular gradation from one class to the other, then it will become very difficult to express a definite opinion as to whether a given sample consists of genuine shark-liver oil or not.

It is obvious, moreover, that a question will be asked which may not be very easy to answer—namely, what is shark-liver oil? It is very clear that, since the two classes of liver oil to which I have referred are very different products, usable for different purposes and probably commanding different prices, shark oil will in all cases have to be bought and sold on the results of analysis.

The spinacene-containing oil can be very readily distinguished from fish-liver oil adulterated by the addition of added hydrocarbons by the high iodine value of the unsaponifiable matter and by the large amount of ether-insoluble bromide formed when it is treated with bromine.

So far as the unsaponifiable matter is concerned, it should be borne in mind that oils of the high specific gravity class containing up to 25 per cent. of unsaponifiable matters are often met with, the unsaponifiable matter in this case consisting largely of alcoholic bodies such as cholesterol.

It was thought that it would be of interest to compare the colour reactions given by the fish-liver oil containing spinacene with those given by an average sample of cod-liver oil. The following are the results:

	Cod-Liver Oil.	Spinacene-Containing Shark-Liver Oil.
One drop of a mixture of one volume of oil with one volume of carbon disulphide was introduced into concentrated sulphuric acid.	Deep violet gradually turning brown.	Brown with a slight violet tinge.
One drop of strong sulphuric acid was added to a solution of 1 drop of the oil in 1 c.c. of chloroform.	Violet-red tint, rapidly changing to rose-red, and finally to yellow-brown.	Green at first, becoming brown.
Two c.c. of a solution of sodium phospho-molybdate acidified with nitric acid were added to a solution of 1 c.c. of the oil in 5 c.c. of chloroform.	Blue-green.	Very faint bluish-green colour.
Ammonia was added to the preceding solution.	Intense blue.	Very pale blue.
Three drops of fuming nitric acid were cautiously added to about 10 drops of the oil.	Red at place of contact, changing to deep pink, and finally to yellowish-brown.	Yellow at place of contact, changing to dirty violet colour.

Spinacene itself does not give any of the above reactions. As might be expected, therefore, the spinacene-containing oil gives the various colour reactions much more faintly than ordinary liver oils.

With regard to the uses to which spinacene, or fish-liver oils containing large proportions of it, may be put, it is too soon to express any opinion, since this can only be determined by experiments on a fairly large scale. It may, however, be permissible to utter a note of warning, since oils containing any considerable proportion of this hydrocarbon would be liable to oxidise with considerable readiness and might be very dangerous if used for such purposes as, for example, the oiling of wool in the manufacture of woollen goods. In this connection I might refer to a note recently published by Fairley and Burrell (*J. Soc. Chem. Ind.*, 1917, **36,** 113), although the oil in that case consisted largely of fatty acids, and could not have contained spinacene.

DISCUSSION.

Mr. J. H. COSTE suggested that possibly specimens of known origin might be obtained through the Natural History Museum, with information which might be of assistance in determining which species of shark yielded this particular product.

Dr. DYER remarked that the most interesting problem in connection with this matter still remained to be worked out—namely, how the fish produced this relatively vast quantity of hydrocarbon, and what was its physiological function after it was secreted.

Mr. P. J. FRYER said that it seemed curious that the saturated hydrocarbon ($C_{30}H_{62}$) obtained from spinacene was a liquid, since a paraffin of that order would have a melting-point of about 62° C. It seemed, therefore, to be ruled out of the saturated hydrocarbons at present known, and was possibly a terpene-like body.

Mr. A. E. PARKES remarked that on reading Mr. Chapman's paper in the Chemical Society's Journal he had wondered whether the peculiarities of the oil might possibly be due to pathological conditions, or to the season at which the fish were caught. The former suggestion Mr. Chapman seemed to have disposed of, but it would be interesting to know if there were any data to show whether the fish produced oil of the same character at different seasons. In thinking of the possibility of a pathological cause he recalled the case of ambergris, a product of fish origin, which seemed to be regarded as a pathological substance. It appeared to consist principally of unsaturated hydrocarbon, which, however, was solid, and not, as in this case, liquid.

The PRESIDENT remarked that the specimens of the oil and of the hydrocarbon which Mr. Chapman had shown might almost be suspected to be of mineral origin from their smell. This reminded him that some years ago, when dissecting a dog-fish, he had found the liver to have a curiously paraffin-like odour.

Mr. CHAPMAN, in reply, said that the odour of spinacene, when fresh, was not in the least suggestive of paraffin, but after distillation there was a faint empyreumatic odour, as was almost invariably the case with all high-boiling hydrocarbons which had been distilled over sodium, no matter how low the pressure or how carefully the distillation had been conducted. On heating the hydrocarbon to a temperature just short of ignition the smell was distinctly resinous, and more suggestive of the terpenes than of the paraffins, although in the case of the saturated hydrocarbon some slight paraffin-like smell was noticeable. It was interesting to hear the President's observation concerning the liver of the dog-fish, and it seemed quite possible that this also contained unsaturated hydrocarbons similar to spinacene. As to which species of sharks yielded oils containing spinacene or similar unsaturated hydrocarbons, all he could say was that the *Spinacidæ* or *Squalidæ* did, and possibly other species might also be found to have the same property. Having dealt fully with the chemistry of the substance elsewhere, he had scarcely touched upon it in the present paper, but in answer to a question it might be mentioned that the hydrocarbon distilled at a constant temperature and formed a number of well-defined derivatives, so that there could be no reasonable doubt as to its individuality. It seemed extraordinary that there should be so large a proportion of one substance in a single organ. The liver of this species of shark was very large, occupying the greater part of the body cavity, and Dr. Mastbaum had referred to the fact that it differed from other livers in being more soft and flabby, so that on merely piercing it with a knife the oil exuded from it freely. The physiological aspect of the matter was very interesting. Of course, it was not possible to say what exact function the hydrocarbon fulfilled in the fish, or how it was formed. One would like to know whether it was capable of being easily oxidised in the cells, and, if that were the case, whether it was not carried straight to the muscles and oxidised there. These fish lived at very great depths, and must need an easily available supply of energy, which a substance like spinacene would no doubt be capable of yielding on oxidation. He was now investigating the effect on it of mild oxidising agents, and possibly this might throw some light on the physiological side of the problem. It was quite clear that the saturated hydrocarbon was not a normal paraffin, since normal paraffins of such high molecular weight were solid. It was unlikely, too, that it was an iso-paraffin. At a temperature as low as - 25° C. it showed no sign of solidifying, and he knew of no iso-paraffin that would remain liquid at that temperature, though, of course, the existence of such a body was conceivable, as the iso-paraffins were almost innumerable. It might be that the formula would have to be revised later on. He expected that spinacene would be found to be an open-chain compound with a ring system in it. That was borne out by a number of observations on the way in which the hydrocarbon was saturated by substances like hydrogen chloride and bromine, and also by the way in which it burned—namely, with a smoky flame and a strong resinous smell. The probable presence of a ring structure was indicated by the fact that spinacene was much more stable than an open-chain molecule with thirty carbon atoms could be expected to be. As to the utilisation of the compound, one might suggest that it could possibly serve as a substitute for turpentine. The sample came to him at the end of September, and the fish were probably caught during the late summer, but he had had no opportunity of studying whether or not the character of the oil varies at different seasons.

* * * * *

NOTE ON THE INFLAMMABILITY OF PETROLEUM SPIRIT AT LOW TEMPERATURES.

By J. H. COSTE, F.I.C.

(*Read at the Meeting, April 4, 1917.*)

Abel's apparatus for the determination of flash-point is not adapted for giving numerical results below a temperature of about 60°. Although in returning the results of statutory testings it is sufficient to describe the flash-point as "below 73° of Fahrenheit's thermometer," cases sometimes arise in which some more definite statement as to inflammability is desirable—*e.g.*, in evidence at coroners' courts.

Ordinary motor-spirit will inflame readily over ice. I have also found, in one instance, that a flash could be obtained from motor-spirit in a small tall beaker over solid mercury—that is, at a temperature of about – 38° C. The "spirit" with mercury under it was cooled in liquid air until both spirit and mercury were solid, and then the beaker was removed from the cooling liquid and a small flame applied to the top of the vessel from time to time. A flash occurred whilst the mercury was still solid, but on inverting the vessel over a dish the mercury fell into the dish as a solid and immediately melted. It is reasonable to conclude that the "open" flash-point was not far removed from – 38° C., the melting-point of mercury.

A priori considerations based on the vapour pressures of the lower liquid members of the paraffin series point to their probable inflammability at very low temperatures.

VAPOUR PRESSURES.

	n-Pentane.	*n*-Hexane.	Di-isopropyl.
– 30° C.	37·95 mm.	6·95 mm.	
– 20° C.	68·85 mm.	14·10 mm.	
– 10° C.	183·25 mm.	25·90 mm.	45·2 mm.
0° C.	183·25 mm.	45·45 mm.	79·95 mm.

In the following experiments the liquids contained in a thin test-tube 100 mm. long and 25 mm. diameter were cooled in liquid air, and then the tube was transferred to an empty Dewar tube, in which it was supported by means of a card with a central circular aperture. The tube was covered with a card and tested with a small flame (of course, removing the cover) at about every 2° C. until it flashed.

The temperatures were determined by means of a copper-eureka thermocouple, with the "hot" junction in ice and water and the "cold" junction dipping about 18 mm. below the surface of the liquid. The thermocouple was calibrated by means of the solidifying points of monobrombenzene – 31·1° C., mercury – 38·8° C., chloroform – 70° C., toluene – 97° C., and by liquid air. A Holden-D'Arsonval mirror galvanometer was used, and the deflections obtained at 1 metre distance were observed.

Pratt's motor-spirit solidified at – 128° C. and flashed at – 30° C. (= –22° F.). (Surface of liquid 18 mm. from top of tube.)

"Standard" spirit flashed at – 11° C. (= +12·2° F.). (Surface of liquid 50 mm. from top of tube.)

"Shell" spirit flashed at – 16° C. (= +3·2° F.). (Surface 50 mm. from top of tube.)

A fairly pure sample of acetone was also examined. This solidified at – 96° C. (pure acetone – 95°) and flashed at – 9·5° C. (= +14·9° F.).

It will be seen from these determinations that ordinary motor-spirit is a dangerous stuff to handle anywhere near naked lights, at any temperature likely to occur in this country; and, on the other hand, that it is not likely to give trouble (as benzene might) by solidifying at any temperature which might be reached near the poles. Wilson, Bowers, and Cherry-Garrard, on the Ross Barrier in the Antarctic, found as low as –77° F., = – 60·5° C. when Dr. Wilson noted. "Our paraffin at these temperatures was easy to pour, though there was just a trace of opalescent milkiness in its appearance."[*] This opalescence is observed in motor-spirit before it becomes a viscous liquid, and then solidifies like paraffin wax.

The inflammability of acetone at low temperatures is rather less than that of the motor-spirit which gave the highest flash.

I regret that I have no details of the other properties of these liquids. The figures, however, appear to be worth placing on record.

TEDDINGTON.

DISCUSSION.

Mr. E. M. HAWKINS said that in attempting recently to determine the flash-points of some mixtures containing petrol, paraffin, and a small quantity of nitro-benzene or nitro-toluene, he had found that with one sample a flash was obtained even below − 5° or − 6° F. In that case the proportion of petrol was only 30 or 40 per cent., and the lowness of the flash-point came to him as somewhat of a surprise. Another sample contained only a very little petrol, but still the flash-point was low—namely, about 40° F.

The PRESIDENT asked whether Mr. Coste's tests were "open" or "closed" tests.

Mr. COSTE said that it was not possible to use the Abel apparatus for low temperatures, but the conditions corresponded as nearly to those of the Abel test as the circumstances allowed. He found it convenient to use one of the short, wide test-tubes devised by Dr. Houston for the *B. coli* test, the tube being covered with a cardboard cover. It was a "closed" test, although not made under any recognised standard conditions, being simply the best that could be done in the circumstances.

⁂

DETERMINATION OF VOLATILE "THINNERS" IN OIL VARNISHES.

BY A. DE WAELE AND F. SMITH, A.I.C.

(*Read at the Meeting, April* 4, 1917.)

OF all the methods suggested for the estimation of the volatile portion of an oil varnish, that of McIlhiney (*J. Amer. Chem. Soc.*, 1895, **17,** 344) is that most generally adopted. This method consists in the steam distillation of the varnish, when, after a suitable amount of water has passed over, the supernatant layer of volatile oil, consisting of turpentine, petroleum spirit, etc., is either run off into a measuring cylinder and its gravity taken, whereby the weight is obtained or weighed in a dried separating funnel. A correction of 0·3 c.c. is allowed for every 100 c.c. of water distilled over.

[*] "Scott's Last Expedition," ii. 17, 462.

Other methods have been suggested (ANALYST, 1916, **41,** 318), but our experience has shown that such procedures, involving as they do loss by evaporation at ordinary or elevated temperatures from thin films, yield results which embody loss by evaporation, together with increase in weight by absorption of oxygen. The employment of such methods furthermore precludes the possibility of examination of the residual combination of gum and oil with a view to proximate analysis, as considerable changes by oxidation would occur.

The steam distillation method of McIlhiney suffers from the drawbacks of the mechanical difficulties of overcoming the slight losses occasioned during the complete collection of the spirit from the condenser, separating funnel, etc. Examination of the residue of fixed oil and gum, although not impossible, is not easy on account of the necessity of breaking up the emulsion which is formed, considerable quantities of ether, etc., being required and a long time being needed for the separation. The method offers the advantage, however, of enabling the volatile solvent removed to be examined and identified, although the value of such knowledge is open to considerable criticism, no satisfactory conclusions as to the relative merits of petroleum spirit and turpentine having been unanimously agreed upon in the trade.

The method we hereby submit permits of rapid and accurate estimation of the volatile solvent. The residual gum and fixed oil, at the same time, are readily obtained in a condition ready for further examination if necessary.

Three to four grams of the varnish are weighed into a CO_2 flask of silica, and 60 to 70 c.c. of boiling water added. This is then boiled over a small free flame until the issuing steam no longer smells of volatile solvent. This usually requires about five minutes. As the dispersion of the spirit proceeds, the liability to froth diminishes and the now more viscous varnish residue partly adheres to the flask and partly coagulates into lumps. We have found it advantageous to weigh a small piece of broken glass along with the flask and impart a continuous brisk rotary motion during boiling, the flask being held in a spring test-tube holder.

The subsequent treatment will depend a great deal on the physical state of the residue. Many varnishes yield a residue so coherent as to permit of the water being poured off without cooling, safety in separation being insured by pouring into a porcelain evaporating dish. Other varnishes, however, require that the contents be cooled under the tap in order to cause a floating layer to adhere to the walls of the flask. The bulk of the water having been removed, a few c.c. of strong alcohol or methylated spirit are added, and the flask is immersed up to the neck in a boiling water-bath. This treatment is repeated similarly with a small quantity of acetone until the residue appears clear and transparent, any cloudiness being indicative of water remaining. Care must be taken to remove the flask from the source of heat as soon as the volatile solvent is evaporated, otherwise, in the absence of alcohol or acetone vapour, oxidation will ensue.

It merely remains to blow out the remaining acetone vapour from the flask with a bellows whilst still hot, then cool and weigh.

Comparative tests of McIlhiney's and our method gave the following results:

No.	McIlhiney's Method. Per Cent.	Gravimetric Method. Per Cent.	Difference.
1	44·9	43·0	1·9
2	43·3	42·0	1·3
3	39·0	37·5	1·5
4	48·6	47·5	1·1
5	52·5	51·0	1·5
6	54·0	52·5	1·5
7	35·5	35·5	0·0

It may be mentioned that in each case with McIlhiney's method an allowance of 2 c.c. per 100 grms. of varnish examined was made—*i.e.*, an addition of 0·3 c.c. of spirit found for every 100 c.c. of water distilled over. This addition was made irrespective of the nature of the distillate, and it is reasonable to suppose that the allowance for solubility of petroleum spirit in water may be less than this.

There is now no difficulty in obtaining satisfactory silica ware for the purposes of this determination, and the initial outlay of the flasks is soon compensated for by the time saved.

DISCUSSION.

Mr. J. H. COSTE asked whether the authors had tried distillation under reduced pressure. He had found that in that way, with care, the distillate could be obtained in a satisfactory condition, while the residue also was available for examination. The results agreed with those obtained by steam distillation, and the solvent was available for examination in either case. As the authors mentioned, however, it was doubtful whether the examination of the solvent was of much value. Mr. W. E. F. Powney, as the result of a large number of experiments which were recorded in a paper on "The Influence of Solvents on the Drying of Linseed Oil" (ANALYST, 1910, **35**, 192-198), had made the following remark: "From the above results it is evident that—with a possible exception in the case of raw oil—neither solvent (*i.e.*, neither turpentine nor turpentine substitute) accelerates the drying of linseed oil to any marked extent; but since the use of a solvent is necessary, if only for thinning, turpentine is on the whole the most suitable for the purpose"; and some work done on the subject by Captain Nash and himself had led to a similar conclusion.

Captain L. M. NASH remarked that one must be careful not to confuse an oil paint with an oil varnish. Whether an oil paint was thinned with turpentine or with a substitute might not make much difference, but with an oil varnish there might conceivably be some physical effect on the "gum," causing the defect known as "blooming."

The PRESIDENT said that he gathered from the paper that in the case of an oil varnish it was the quantity of thinner present, rather than its nature, that determined the value of the varnish.

Mr. DE WAELE said that, except in varnishes used for preparation work ("goldsize"), in which there must be a high percentage of thinner, and consequently a low viscosity, in order to insure penetration and rapid evaporation, the average proportion of spirit in the varnish was comparatively constant within the limits of, say, 40 and 50 per cent. The percentage of spirit, however, and the viscosity of the residue of oil and gum might afford some clue as to the method of manufacture (degree of polymerisation of the oil).

They had tried distillation under reduced pressure, but had found it to be troublesome, owing to frothing, etc., and, moreover, to show no advantage over McIlhiney's method.

The question of the comparative value of turpentine and turpentine substitutes was still being discussed in trade societies, but so far as his experience went the only reason for the use of turpentine seemed to be that it was demanded by the consumers, probably on account of the pleasant smell it conferred to the varnish.

The question of the solvent in regard to "blooming" in the dried film was also under discussion, and it appeared to be generally thought that this was caused by the use of petroleum spirit, but he did not think that this had been really proved. In a good many cases, however, the petroleum spirit seemed to act less efficiently as a solvent of the gum, particularly in "polishing" varnishes—*i.e.*, those very rich in gum—and if the amalgamation of the gum and oil were not very thorough—and this was always a difficult matter—subsequent partial precipitation of the gum during addition of the spirit would occur, resulting in a "bloom" on the finished film. In a good many cases within his experience, however, "blooming" was due to the indiscriminate use of such progressive and powerful driers as those of cobalt.

* * * * *

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Detection and Estimation of Added Alkali in Cocoa. X. Rocques. (*Ann. Falsific.*, 1917, **10**, 14-17.)—It is recommended that estimations be made of the total ash, soluble and insoluble ash, alkalinity of the soluble ash, and of the quantity of phosphoric acid in the soluble ash. The following table gives the results of analyses of pure cocoa and of the same mixed with various quantities of potassium carbonate, all the figures representing percentages on the dry, fat-free substance:

	Soluble Ash.	*Insoluble Ash.*	*Alkalinity of Soluble Ash as K_2CO_3.*	*P_2O_5 in Soluble Ash.*
Pure cocoa	2·8	4·4	1·6	0·4
Do., +1 per cent. K_2CO_3 ..	4·0	4·3	2·7	0·5
Do., +3 per cent. K_2CO_3 ..	6·5	3·5	4·8	0·7
Do., +5 per cent. K_2CO_3 ..	8·8	3·4	6·6	1·0

The alkalinity of the ash was estimated with the use of tropeolin as the indicator. The ratio of the soluble to insoluble ash approaches unity in the presence of 1 per cent. of added alkali, and falls below unity as the alkali is increased, whilst the alkalinity and phosphoric acid content of the soluble ash increase. W. P. S.

Alkalinity of Cocoa. Arpin. (*Ann. Falsific.*, 1917, **10**, 10-14.)—According to French law, the alkalinity of the ash of pure cocoa must not exceed 2·75 per cent., expressed as potassium carbonate and calculated on the dry, fat-free substance; if this limit of alkalinity is exceeded, the cocoa must be sold as "solubilised" cocoa to indicate that it has been treated with an alkali during manufacture. Three samples of cocoa examined recently by the author were found to have alkalinities of 3·49, 3·16, and 3·25 per cent., respectively. These cocoas were declared by the manufacturer to be pure and free from added alkali. Analyses of cocoa beans from various sources showed that, in some cases, the alkalinity of the ash does exceed the above-mentioned limit of 2·75 per cent. For instance, for Madagascar beans it was 3·53, and for Chuao beans 3·50 per cent. There is, therefore, reason to believe that the slight excess of alkalinity exhibited by the three samples was due to natural causes. W. P. S.

Cyanogenetic Beans. Kohn-Abrest. (*Ann. Falsific.*, 1917, **10**, 17-19.)—Beans of the *Phaseolatus lunatus* species may be divided into two groups. In the first group are included Java, Kratock, Amer, and Achery beans: these beans yield from 0·05 to 0·25 per cent. of hydrocyanic acid, and they should not be used as foods either in their raw or cooked condition. The other group comprises Cape, Lima, Sieva, and Burma beans, which yield only small quantities of hydrocyanic acid; under strict control, these beans might be used for human consumption. W. P. S.

Tests for Certain Narcotic and Anæsthetic Drugs. E. H. Hankin. (*Indian J. Med. Research*, 1916, **4**, 237-255.)—*Nitric Acid Test:* The substance is just moistened with nitric acid in a porcelain basin which is then heated over a flame, and water is added to the mixture. Cycloform gives a pale yellow colour in the cold, the colouring deepening and changing to black on heating and forming a black oily liquid. Holocaine is at first colourless, and then gives a pale reddish-brown colour. Orthoform turns black immediately, the colour changing rapidly to dark brown. Antipyrin turns yellow and becomes black on heating, the mass eventually deflagrating and emitting a white vapour with an odour similar to that of isocyanide. If the nitric acid is added in larger quantity, and the mixture is warmed, the yellow colour first produced changes to crimson. This reaction is given by antipyrin adulterated with 50 per cent. of cocaine. Diamorphine (heroine) gives a yellow coloration with a little nitric acid, and a bright green coloration when the acid is added in excess. *Permanganate Film Test:* In addition to cocaine and its substitutes (ANALYST, 1911, **36**, 2), eighty other drugs and alkaloids were subjected to this test. Crystals were only formed by atropine, hydrastine, and scopolamine, all of which turned brown more or less rapidly. Red oily globules which speedily became brown were given by atropine and pilocarpine. If too much cocaine has been used for the test, crystals may not be obtained. In such a case the addition of another drop of alum solution will cause the crystals to appear. *Fehling's Solution:* Anæsthetin in 0·5 per cent. hydrochloric acid gives with Fehling's solution a white precipitate which, after a few minutes, will form rod-like crystals. Cocaine, alypine, eucaine (alpha- and beta-), novocaine, stovaine, and tropococaine, give a white precipitate composed of oily drops. Brucine and strychnine give white crystalline precipitates with Fehling's solution, but do not show the change in form exhibited by anæsthetin. Granular white precipitates are given by acoine, aconitine, cycloform, holocaine, quinine, quinine-urea, and yohimbine, and a yellow or greenish-yellow precipitate by chloretone and brometone. No precipitate or only a faint turbidity is produced by acetanilide, antipyrin, aspirin, benzosol, bromural, caffeine, chloral, chloralamide, chloralose, chloralurethane, codeine, hedonal, morphine, heroine, phenacetin, salicin, salicylic acid, salol, santonin, sodium-veronal, sulphonal, tetronal, thiocol, trional, urethane, urotropin, and veronal (barbitone). Orthoform yields a yellowish or greenish-yellow turbidity, the liquid becoming transparent and sage-green after a short time, and then, after some hours, assuming a reddish tint. *Effect of Melting:* In certain cases the appearance of the substance after melting and cooling on a glass slide has a distinctive appearance. For example, the crystalline film may show a pearly appearance, as in the case of anæsthetin, aspirin, sulphonal, tetronal, trional, veronal, etc. Or the film may contain minute oval spaces in rows (cycloform, anæsthetin). *Sulphuric Acid* and *Potassium Iodate Test:* The substance is moistened with 10 drops of strong sulphuric acid and a crystal of potassium iodate is added. (1) If no colour develop the dish is warmed till vapours appear—(*a*) Brown olive green with blue and violet streaks, usually changing to dirty violet: *cocaine, eucaine, tropococaine.* (*b*) Brown to dirty brown: *novocaine.* (*c*) Reddish, then deep brown: *anæsthetin.* (2) If the colour appear more or less quickly in the cold—(*a*) Slowly, reddish or brownish-yellow, then on heating giving brown olive and blue-green streaks: *alypine.* (*b*) Raspberry-red with yellow and brown streaks, fading to purple grey and becoming red on heating: *stovaine.* (*c*) Immediately brown-red; no change on heating: *holocaine.* (*d*) Immediately brown-red, turning brown on heating: *nirvanine.* (*e*) Immediately brown- red, then deep green; on heating, brown-red: *acoine.* (*f*) Blue-green, changing to blue-violet; on heating, red: *orthoform.* Benzoic acid shows a play of colours similar to those given by cocaine in this test. *Urotropine Test* (ANALYST, 1914, **39**, 481): Cocaine gives a faint brown coloration with purplish tint, changing rapidly to deep brown, but the test is not distinctive, since similar colorations are given by eucaine and tropococaine. Saporetti's bromine test is also useful for distinguishing the cocaine substitutes and other drugs (see ANALYST, 1911, **36**, 2). C. A. M.

Nitrogen in Amino Form as estimated by Formol Titration, in Relation to some other Factors measuring Quality in Wheat Flour. C. O. Swanson and E. L. Tague. (*J. Amer. Chem. Soc.*, 1917, **39**, 482-491.)—In previous work by one of the authors and Willard (ANALYST, 1912, **37**, 190) it was shown that a slight increase in flour of nitrogen in amino form gave a greater loaf volume, but a large increase was prejudicial in every way. The addition of amino compounds to the flour in the form of pure chemicals was also harmful to the resulting bread, although some ammonium salts, notably the chloride, were useful. A comparatively large percentage of ash and acidity does not by itself denote unsoundness in a flour. Since the bran and shorts contain ten times as much ash and acidity as the flour, the presence of a small amount of bran will greatly increase the ash and acidity values. The amount of amino compounds in flour made from germinated wheat was found to increase proportionately to the length of time the wheat had germinated. In the total wheat the percentage of amino compounds was found on an average to be about 0·53 per cent., in the patent flour made from it 0·162, in the "clear" grade 0·270, and in the low grade 0·396 per cent. The Sörensen titration method (*J. Amer. Chem. Soc.*, 1916, **38**, 1098-1109) employing 0·05 N baryta was used for the titrations, water and flour being mixed in the proportion of 10 to 1, and kept in a water-bath for two hours at 40° C. The mixture was shaken once every fifteen minutes and finally filtered. Portions were then titrated for the first and second stage, which measure acidity and amino-acids respectively. Titratable nitrogen is more uniformly distributed in the wheat kernel than are the materials which determine the amount of ash and acidity; therefore in lower grade flours, as compared with patent made from the same sound wheat, the increase in titratable nitrogen is not proportional to the increase in ash or acidity. The titratable nitrogen, since it measures certain protein cleavage products, is a measure of the extent to which proteolytic action has advanced in a flour over and above the amino-acids normal to a sound flour. The lower grades of flour made from sound wheat do not contain nitrogenous substances, such as are measured by the formol titration, in as large a proportion as ash and acidity. H. F. E. H.

Rapid Estimation of Oil in Malt and Cod-Liver Oil Preparations. H. D. Richmond and F. G. Hitchman. (*J. Soc. Chem. Ind.*, 1917, **36**, 273.)—The method depends on the fact that whilst the density of cod-liver oil is less than that of water, that of malt extract is considerably greater; and, further, that the density of a 50 per cent. solution of malt extract is, within small limits of error, proportional to the refractive index of malt extract itself. It has also been observed that small solid particles or small globules of oil do not affect the refractive index. Equal weighed quantities of the sample and of distilled water are mixed, and the density determined at 20° C. by means of a delicate hydrometer, the temperature correction being 0·0006 for 1° if the determination be not made precisely at 20° C. The refractive index is determined at 20° C., preferably by the Abbé refractometer, correcting the reading, if necessary, for small differences of temperature by adding 0·00018 for each 1° above. The percentage of oil is calculated by the following formula:

$$(n_D - 1{\cdot}3332) \times 549{\cdot}6 - \frac{d-1}{d} \times 584{\cdot}8.$$

The worst of four test numbers given is 29·4 per cent. oil found when 29·8 per cent. was present. G. C. J.

Italian Oil of Turpentine from Pinus pinaster. M. Palazzo. (*Annali Chim. Applic.*, 1917, **7**, 88-94.)—The normal Italian oil of turpentine is a mixture of the oils derived from *Pinus pinea* and *P. pinaster*. A typical sample had the following characters: Sp. gr. at 15° C., 0·863; at 25° C., 0·855; $[n]_{D\ 25^\circ C.}$=1·4678; $[\alpha]_D$= −48·15° ; flash-point, 35·5° C.; and solubility in 90 per cent. alcohol, 1 : 5·1 at 23° C. Eighty per cent. of the oil distilled between 155° and 165·5° C., whereas ordinary oils of turpentine yield 90 per cent. of distillate between 155° and 163° C. The first fraction distilling up to 159° C. had a sp. gr. of 0·8576 at 20° C., $[n]_{D\ 25^\circ C.}$ =1·4653 and $[\alpha]_D$=−46·54°. Two pure commercial samples derived from *P. pinaster* had the following characters:

Sp. gr. at 15° *C.*	*Sp. gr. at* 25° *C.*	n^{20}_{D}.	n^{25}_{D}.	$[\alpha]_D$.	*Flash-point.* ° *C.*
0·867	0·8595	1·4700	1·4683	−35 at 26° C.	33·5
0·871	0·863	1·4707	1·4690	−35 at 23° C.	33·5

These values agree with those given by the best French oil of turpentine, which begins to boil at 154° C., and between that temperature and 163° C. yields 85 to 90 per cent. of distillate. The only particular in which the Italian oils differed from the French product was in the higher values for $[\alpha]_D$, which in the latter case ranges from −29° to −33°. The higher rotatory power of the Italian oil is due not only to pinene, but to a large extent to *l*-limonene. C. A. M.

Chemical and Physiological Detection of Several Alkaloids in the Same Solution. E. Philippi. (*Arch. Farm. Sperim.*, 1916, **22**, 120-130; through *J. Chem. Soc.*, 1917, **112**, ii., 56.)—The characteristic reaction of strychnine with sulphuric acid and potassium dichromate is not shown by 1 mgrm. of strychnine nitrate in the presence of 0·04 grm. or more of quinine bisulphate, a transitory garnet-red coloration being produced, which becomes green or greenish-grey; with smaller quantities of quinine the reaction is distinct, but transient. The same effect is observed when salts of the alkaloids with the same acid or the free alkaloids are used. Crystals of strychnine picrate can be obtained in the presence of a large excess of quinine, but they are not then characteristic. The alkaloids are most simply and certainly separated by the use of sodium potassium tartrate; quinine tartrate is insoluble in solutions of alkali sulphates and tartrates, whereas the strychnine salt is soluble. Mixtures which do not give the characteristic reaction with potassium dichromate do not cause the characteristic symptoms in the frog.

Estimation of Nicotine in Tobacco. A. Tingle and A. A. Ferguson. (*Trans. Roy. Soc. Canada*, 1916 [iii.], **10**, 27-31; through *J. Chem. Soc.*, 1917, **112**, ii., 55-56.)—The authors have worked out the following method for the estimation of nicotine in tobacco. A mixture of 20 grms. of tobacco, 40 grms. of barium hydroxide, and 150 c.c. of water, is distilled with steam into a 500 c.c. flask until the distillate gives no alkaline reaction with phenolphthaleïn. To the distillate 20 c.c. of sulphuric acid are added, and the liquid evaporated to about 50 c.c. This solution is made strongly alkaline with potassium hydroxide, a few drops of baryta water being added for clarification. The solution is then made up to 100 c.c., the precipitate allowed to settle, the supernatant liquid filtered, and its rotation then determined in the polarimeter. In a modification of the method the nicotine is extracted from the steam distillate by chloroform. These two methods gave concordant results, higher than those obtained, using the same specimen of tobacco, by the methods of Toth and of Kissling.

Estimation of Antipyrine. M. Francois. (*J. Pharm. Chim.*, 1917, [vii.], **15**, 97-105.)—The volumetric method proposed by Bougault (ANALYST, 1898, **23**, 93) is reliable. In this process 20 c.c. of an alcoholic 1 per cent. solution of the sample are mixed with 20 c.c. of mercuric chloride solution (2·5 grms. per 100 c.c. of alcohol), and the mixture is titrated with iodine solution (1·351 grms. per 100 c.c. of alcohol). The number of c.c. of iodine solution used is multiplied by 5 to obtain the percentage quantity of antipyrine. As, however, the iodine solution decreases in strength when kept, it is advisable to standardise it against pure antipyrine every time it is used. Bougault has also described a quantitative method for the approximate estimation of antipyrine; the latter is precipitated from its aqueous solution as iodo-antipyrine in the presence of sodium acetate, and the precipitate is collected and weighed. The author finds that this method is quite untrustworthy, although it has been adopted by the French Codex. W. P. S.

ORGANIC ANALYSIS.

Detection of Hydrocyanic Acid. G. W. Anderson. (*J. Soc. Chem. Ind.*, 1917, **36**, 195-196.)—The silver nitrate test gives a definite precipitate with solutions of potassium cyanide stronger than 0·01 per cent., but with weaker solutions only an opalescence, the limit being reached with a 0·0001 per cent. solution, when the opalescence can only be detected against a black background.

The Prussian blue test readily detects 0·001 per cent., the thiocyanate test 0·0001 per cent. The latter test is best conducted as follows. To the aqueous solution of hydrocyanic acid or alkali cyanide sufficient yellow ammonium sulphide is added to impart a yellow colour. A few drops of alkali hydroxide are added and the mixture evaporated to dryness. The residue is dissolved in water with the addition of a little hydrochloric acid, this being necessary to destroy thiosulphate produced in the process. Ferric chloride solution is finally added and sufficient time allowed for the colour to develop in very dilute solutions.

The picric acid method is condemned, not only on account of the ambiguity of the results, due to the fact that it merely proves the presence of a reducing substance, but because the sensitiveness of the test is too dependent on the exact experimental conditions.

The guaiacol test is far more sensitive (it reacts with 0·00001 per cent. solutions of potassium cyanide), but, being disturbed by cigar-smoke, ammonia, and other substances, can only be used as a preliminary test in conjunction with the Prussian blue or other specific test. G. C. J.

Determination of Lævulose in Presence of Dextrose. L. Loewe. (*Proc. Soc. Exper. Biol. and Med.*, New York, 1916, **13,** 71-72 ; through *J. Chem. Soc.*, 1917, **112,** ii., 49.)—The method depends on the yellow coloration developed after boiling and addition of a 0·2 per cent. solution of orcein and a 85 per cent. solution of phosphoric acid; the yellow colour becomes orange on addition of alkali. The test is made quantitative by colorimetric comparison with a standard lævulose solution treated with the reagents. Lævulose was detected in 1 c.c. of a 0·05 per cent. solution. Cane-sugar interferes, owing to hydrolysis by the acid.

Importance of the Varrentrapp Reaction in Fats and Soaps. W. Schrauth. (*Deutsch Parf. Zeit.*, 1916; through *Chem. News*, 1917, **115,** 114.)—The Varrentrapp reaction, whereby oleic acid is converted into palmitic and acetic acids with evolution of hydrogen by fusion with an excess of alkali hydroxide, is capable of general application for the preparation of saturated fatty acids from unsaturated, and might conceivably serve as an alternative to the largely practised hydrogenation process. The reaction may be expressed by the equation:

$$C_{17}H_{33}COOH + 2KOH = C_{15}H_{31}COOK + CH_3COOK + H_2.$$

In a general sense, for each double bond, two carbon atoms are split off in the form of acetic acid, so that in the case of clupanodonic acid, $C_{18}H_{28}O_{27}$ (the main constituent of all train oils and the source of the objectionable train-oil smell), containing four double bonds, the ultimate product is capric acid, $C_{10}H_{20}O_2$. The product resulting from the alkali fusion of train-oil fatty acids shows a certain resemblance to coconut-oil soap. After acidification, a perfectly white fatty acid may be distilled; the yield usually amounts to about 85 per cent. of the original fatty acids, with a loss of 10 to 12 per cent. as acetic acid and 3 to 5 per cent. as distillation residue. The melting-point of the fatty acids lies between 35° and 40° C., and the iodine value is greatly reduced. The fusion is carried out in an autoclave of 5,000 litres capacity charged with 2,500 kilos of train-oil fatty acid and 700 to 800 kilos of commercial caustic soda dissolved in an equal weight of water. The mass is heated to about 200° C., rising to 260° C. in about six hours, the pressure not being allowed to exceed 10 atmospheres. Train oils treated by the hydrogenation process yield products of the consistence of tallow, but by the Varrentrapp reaction deodorised products are obtained applicable as substitutes for vegetable fat.

J. F. B.

INORGANIC ANALYSIS.

Estimation of Chromium in Ferrochrome. W. Herwig. (*Stahl u. Eisen*, 1916, **36,** 646-650; through *J. Chem. Soc.*, 1917, **112,** ii., 104-105.)—The volumetric estimation of chromium in ferrochrome by means of potassium permanganate gives low results if the theoretical titre number for chromium as recorded in the textbooks (0·310 instead of the empirical number 0·3165) is used. On the other hand, accurate results are obtained by the sodium thiosulphate and potassium dichromate methods. The following shortened sodium thiosulphate process gives results accurate to 0·3 per cent., and can be completed in an hour. The powdered sample is passed through a sieve of 2,700 meshes to the sq. cm., and 0·5 grm. is fused in an iron crucible with sodium peroxide (5 to 6 grms.), gentle heating being used for about a minute until the metal has dissolved in the fused mass, after which it is heated, with gentle agitation, for two minutes with the full Bunsen flame. The somewhat cooled crucible is transferred to a beaker containing about 350 c.c. of water at 60° to 80° C., the beaker immediately covered with a clock-glass, and the water cautiously boiled for five minutes to decompose the sodium peroxide completely; after being cooled the solution is diluted to 500 c.c. and passed through a double filter. 100 c.c. of the filtrate is diluted to about 300 c.c. with water, treated with potassium iodide (1 grm.) and hydrochloric acid (sp. gr. 1·124, 40 c.c.), and, after one minute, titrated with sodium thiosulphate. Decomposition of ferrochrome by magnesium carbonate mixture is frequently incomplete. After being sifted the specimen should be ground for two or three hours in an agate mortar, and the mixture must be heated for at least an hour with a powerful blowpipe flame. The residue from the first operation must be similarly treated at least once more.

Estimation of Chromium in Ferrochrome, Steel, Slags, etc., by the Permanganate Method. P. Koch. (*Chem. Zeit.*, 1917, **41**, 64.)—A quantity of about 0·25 grm. of the finely divided sample is fused for twenty minutes with 4 grms. of sodium peroxide in a porcelain crucible. The fused mass, when cold, is boiled with water until all the peroxide has been decomposed (this requires about thirty minutes, or longer); the solution is then cooled, sulphuric acid is added to dissolve the ferric hydroxide, and an excess of standardised ferrous sulphate is introduced, the excess being titrated with permanganate solution. The ferrous sulphate solution may be standardised against *N*/10 potassium dichromate solution (4·9033 grms. per litre); each c.c. of this solution is equivalent to 0·001733 grm. of chromium.

W. P. S.

Estimation of Small Quantities of Cobalt. A. D. Powell. (*J. Soc. Chem. Ind.*, 1917, **36**, 273-274.)—The solubility of cobalt ammonium thiocyanate in amyl alcohol, with the formation of an intense blue colour, has long been made use of for the detection of cobalt in nickel salts. The author has determined conditions under which the method may be made the basis of an accurate colorimetric method for the quantitative estimation of cobalt. The first necessary condition is the use of a concentration of at least 25 per cent. of ammonium thiocyanate; the second, the use of sodium pyrophosphate avoids ferric iron and the need for filtration of the amyl alcohol solution, as the coloured compound is adsorbed by filter-paper. This last fact makes it inadmissible to precipitate iron as is done in the usual qualitative test, as the amyl alcohol solution always carries enough ferric hydroxide in suspension to render the colour greenish, and filtration is out of the question. The use of pyrophosphate satisfactorily avoids the formation of ferric thiocyanate, and no precipitate is formed. Concentrated thiocyanate solution is added to the solution to be tested, so that the mixture contains about 30 per cent. of ammonium thiocyanate; about 0·5 grm. pyrophosphate is added, the colour is then extracted with two portions of amyl alcohol, and the solution matched against standards. Not more than 0·5 mgrm. of cobalt should be present, or the colour is too intense for accurate comparison. G. C. J.

Estimation of Fluorine in Soluble Fluorides. J. G. Dinwiddie. (*Chem. News*, 1917, **115**, 149-151; from *Amer. J. of Science*, 1917, **42**, 464.)—The solution of the fluoride, which should occupy as small a volume as possible (30 to 40 c.c.), and should be neutral, is heated to boiling, and powdered calcium sulphate is added. After standing for an hour with frequent stirring, the precipitate of calcium fluoride and sulphate is washed by decantation, and then filtered off on a Gooch crucible, with a single disc of filter-paper (no pulp or asbestos), using gentle suction. As calcium fluoride is appreciably soluble, the precipitate is washed with a saturated solution of calcium fluoride and sulphate. It is then transferred by means of a jet of water to an ordinary platinum crucible, the paper disc is incinerated on the crucible lid, and the contents of the crucible are evaporated to dryness and dehydrated by heating to 300° C. This is conveniently accomplished by placing the crucible on a small triangle on a piece of asbestos contained in the bottom of a 3-inch iron crucible, and heating the bottom of the latter to low redness for an hour. Dried in this way, the precipitate readily yields to the subsequent treatment. The cooled crucible and its contents are weighed, the fluoride is decomposed by means of sulphuric acid, and the excess of sulphuric acid driven off by applying heat to the lid of the crucible with a Meker burner. The increase of weight, due to conversion of calcium fluoride to calcium sulphate, is the measure of the fluorine present, 0·58 grm. increase corresponding to 0·78 grm. calcium fluoride or 0·84 grm. sodium fluoride. G. C. J.

Volumetric Analysis of Hypochlorite Solutions used for Sterilising Water, and a Rapid Method for the Estimation of Hydrogen Peroxide. A. Bury. (*J. Pharm. Chim.*, 1917, **15**, 189-193.)—This method for the estimation of available chlorine in hypochlorite solutions depends on the reaction between hypochlorites and hydrogen peroxide according to the equation: $NaOCl + H_2O_2 = NaCl + H_2O + O_2$. The volume of the oxygen is equal to that of the chlorine obtained when the hypochlorite is treated with hydrochloric acid. Conversely, the reaction may be used for the estimation of hydrogen peroxide. In the case of hypochlorite solutions, a measured quantity of the solution is placed in a graduated tube provided with a bulb, water is added, and then hydrogen peroxide up to a definite volume; the tube is now closed with the finger, the contents are mixed by inverting the tube, and, when the reaction is over, the finger is removed slightly so that a portion of the liquid escapes and equalises the pressure. The volume of the liquid remaining in the tube is then noted, and the volume of the liquid which has been forced out is thus found; the latter volume is equal to that of the oxygen produced and also to that of the available chlorine. The tube may be so graduated that the readings give directly the strength of the hypochlorite solution in chlorine units. W. P. S.

Estimation of Small Quantities of Iron and Aluminium (in Foods, etc.). R. Berg. (*Chem. Zeit.*, 1917, **41**, 50-52.)—After the organic matter of the substance has been destroyed by heating with sulphuric acid and nitric acid the acid solution is rendered ammoniacal, then just acid with hydrochloric acid, ammonium acetate is added, and the solution is boiled. The precipitate formed is collected, washed with hot dilute ammonium sulphate solution, then dissolved in hydrochloric acid, and the precipitation repeated as described. After the precipitate has again been dissolved in hydrochloric acid, ammonia is added, the solution boiled, and the precipitate of iron and aluminium phosphates and silica is collected, washed, ignited, and weighed. The ignited residue is then fused with potassium hydrogen sulphate to dissolve the iron and aluminium phosphate, and the insoluble silica is collected and weighed. The iron and aluminium in the solution are precipitated as hydroxides by the addition of ammonia; the precipitate is collected, dissolved in hydrochloric acid, the solution transferred to a stoppered flask, zinc chloride is added, the mixture is rendered alkaline with sodium hydroxide, then just acid with hydrochloric acid, and, after the addition of potassium iodide, the mixture is heated at 65° C. for twenty minutes (the flask being closed), and the liberated iodine is titrated with *N*/250 thiosulphate solution. One atom of iodine corresponds with 1 atom of iron; the quantity of aluminium present is found by difference.

W. P. S.

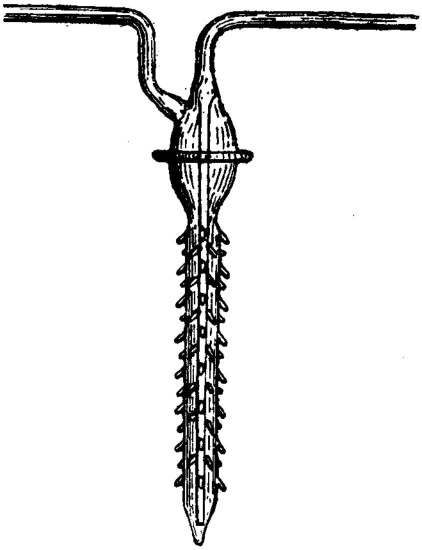
Rapid Method for the Estimation of Magnesium. N. Busvold. (*Chem. Zeit.*, 1917, **41**, 42.)—A volumetric method is described for the estimation of magnesium in limestone. From 5 to 10 grms. of the mineral are calcined in an electric furnace, then dissolved in the least possible quantity of hydrochloric acid, and the solution is boiled. An excess of calcium carbonate is now added, the mixture is boiled, filtered, and the insoluble portion washed. The filtrate is boiled with the addition of 20 c.c. of 6 per cent. milk-of-lime, then cooled, the precipitate is collected on a filter and washed with water containing calcium hydroxide. The filter and precipitate are placed in a flask, and boiled for five minutes with 300 c.c. of water and 40 c.c. of *N*/1 oxalic acid solution; the mixture, while hot, is filtered and the precipitate is washed with hot water. The filtrate now contains the magnesium oxalate together with an excess of oxalic acid; after cooling, the solution is titrated with *N*/5 sodium hydroxide solution to obtain the amount of the free oxalic acid, methyl-red being used as the indicator. The neutral solution is acidified with 25 c.c. of dilute sulphuric acid, heated at 70° C., and titrated with *N*/5 potassium permanganate solution. This titration gives the quantity of total oxalic acid, and the difference between the amounts of total and free oxalic acid gives the quantity of the acid combined with the magnesium; 1 c.c. of *N*/5 oxalic acid is equivalent to 0·004306 grm. of magnesium oxide. W. P. S.

Estimation of Nickel in the Presence of Zinc and Iron. S. Rothschild. (*Chem. Zeit.*, 1917, **41**, 29-30.)—The electrolytic deposition of nickel from an ammoniacal solution is quantitative when the solution contains only iron and aluminium (in addition to the nickel), but the deposition is incomplete when zinc or a large quantity of manganese is present. Further, deposition of nickel from a hot solution containing sodium sulphite is inaccurate in the presence of cobalt. Nickel may be separated, however, by precipitation with dimethylglyoxime, but iron, if present, is also precipitated even from a solution containing a large quantity of tartaric acid. In such cases the nickel may be separated from the iron by dissolving the precipitate in hydrochloric acid, boiling the solution for a few minutes with the addition of hydrogen peroxide, then adding an excess of ammonia, and depositing the nickel electrolytically from this solution. W. P. S.

Estimation of Ozone. David. (*Comptes rend.*, 1917, **164**, 430-431.)—A solution of iron ammonium sulphate containing free sulphuric acid is rapidly oxidised by ozone, but is not affected by ordinary air. For the estimation of ozone in air a litre flask is filled with water, and emptied in the atmosphere to be tested; 5 c.c. of $N/10$ ferrous ammonium sulphate solution (3·92 grm. per litre), containing 20 c.c. of pure sulphuric acid (sp. gr. 1·84), are then introduced, the flask closed and shaken for two or three minutes, and the unoxidised iron salt titrated with $N/10$ potassium permanganate solution. For the estimation of ozone in more concentrated form a solution of acidified ferrous ammonium sulphate containing 39·20 grms. per litre is used, and the liquid afterwards titrated with potassium permanganate solution containing 3·16 grms. per litre. Five c.c. of the dilute reagent correspond with 0·04 c.c. of oxygen. C. A. M.

Detection of Phosphorus by Dusart and Blondlot's Method, and its Application to Toxicology. Preparation of Pure Zinc for the Detection of Phosphorus and Arsenic. H. J. Lemkes. (*J. Pharm. Chim.*, 1917, **15**, 177-188.)—This method, in which phosphites, hypophosphites, etc., are reduced to phosphorus hydride by the action of zinc and hydrochloric acid, is capable of detecting as little as 0·0025 grm. of phosphorus in the form of hypophosphite, or 0·075 mgrm. in the form of calcium phosphite, provided that the phosphorus hydride is passed into silver nitrate solution, the precipitate collected, and again treated with zinc and hydrochloric acid. The reduction is somewhat slow, and is best carried out at a temperature of about 55° C. There is no appreciable oxidation of the phosphorus hydride by the excess of silver nitrate, and the use of the spectroscope offers no advantage over that of the naked eye in observing the characteristic colour of the hydrogen flame containing phosphorus hydride. The presence of sulphurous compounds and of alcohol interferes with the method, and in this case the Mitscherlich method should be used. In poisoning with phosphorus, the latter remains unchanged in the body for some months, and may be detected by the method; the author has never obtained a positive reaction from animal organs in the absence of phosphorus. Hehner's method (ANALYST, 1902, **27**, 261) of preparing zinc free from arsenic (by fusion with the addition of sodium) also removes any phosphorus from the metal. W. P. S.

APPARATUS, ETC.



Movable Condenser. Vigreux. (*Bull. Soc. Chim.*, 1917, **21**, 46-48.)—The condenser shown in the illustration is made entirely of glass; it may be suspended in the neck of a flask by means of the annular projection round the bulb, and serves all the purposes of a reflux condenser. The part of the condenser below the bulb is about 10 cm. in length. W. P. S.

Analytical Chemistry and its Future. W. F. Hillebrand. (Chandler Lecture, Columbia Univ., U.S.A.; through *Chem.* (*News*, 1917, **115**, 109-112, 122-124, 137-139. —The comparative neglect of the science of analytical chemistry in academic and industrial circles is much to be deplored, because problems involving the highest analytical skill and thought are constantly developing, both in connection with research in physical chemistry and in the study of the influence of rare elements and of minute impurities on the commercial value and industrial utility of raw materials and manufactured products. In electro-chemistry there is a similar need for exact analytical data, as, for instance, in the electro-deposition of silver, which forms the basis of the ampère; and in nickel plating on a commercial scale, where the character of the plating is subject to the influence of very minute additions. The lecturer pointed out that many publications of new analytical methods are open to the criticism that they are not thoroughly worked out in all possible aspects of the particular problem involved, and especially that the results are generally obtained with considerable quantities of the element sought, without due regard to possible disturbances produced by the preponderating presence of other elements. For much of the unsatisfactory condition of fine analytical work the educational institutions are responsible, in that accurate analytical training is not taught as a science in itself. In certain lines of work some improvement is to be noted of recent years, but, as a general rule, the young chemist from academic institutions is characterised by a comparative lack of sound and comprehensive knowledge of the principles on which analytical chemistry is based. So far as training is concerned, the appointment of more experienced specialists as teachers, together with a modification of the curriculum in the desired sense would correct the fault to a large extent. A second line on which the deficiency may be attacked is in the extended use of certified analysed reagents. A strong movement in favour of the use of reagents of definitely ascertained purity has been fostered by the U.S. Bureau of Standards, not merely in order to supply the analyst with reagents which he may employ with confidence, but with the far more important object of affording him standard substances with which he may measure his analytical skill and the soundness of his methods against results ascertained by several specialists in the branch in question. Especially as regards materials employed in the iron and steel industries, standard reagents and raw materials are issued which have been analysed by several of the most skilful specialists in the subject; and if an analyst can obtain results comparable with those marked on the sample, he may be satisfied that his methods and his technique are reliable in connection with other materials of similar type. In preparing these standards, much valuable analytical research has been done, and many unsuspected sources of error have been detected and overcome. The discussion of standard analysed materials naturally leads to that of standard methods of analysis, in which direction America has taken a prominent lead. Such methods are, in the main, commercial methods, and absolute accuracy must sometimes be subordinated to rapid and simple procedure. The conditions laid down for a standard method are: (1) Its limits of accuracy and its applicability must be clearly defined and understood; (2) it must yield sufficiently accurate and concordant results in the hands of different analysts; (3) it should not demand such close adherence to detail or such manipulative skill, time, and judgment as seriously to affect its utility; (4) it should have been tested on material of high purity or such as has been carefully analysed by independent and reliable methods; (5) the results obtainable on a given class of material (steel, iron, etc.) should not be too dependent upon the composition. These principles have not always been rigidly observed, but a standard method is not intended to be permanently invariable, and, if its limitations be well understood, even an imperfect method is better for commercial purposes than a variety of methods of uncertain relative and even absolute merit. Committee work, for a variety of reasons, is not always so satisfactory as might be expected, and this field of work is best undertaken by a permanent institution commanding the services of men of high qualifications and large experience, to which should also be entrusted the preparation and control of standard samples of commercial articles and of pure reagents for fine analytical work. Such an institution should also be in close touch with industrial circles, and might undertake referee work in connection with commercial disputes and the recording and investigation of developments in analytical chemistry. The activities of the institution might therefore be classified under the headings: research work, referee work (including standard chemicals), and educational work. The prestige attaching to direct Government control is a strong argument in favour of the establishment of a national institution with the Bureau of Standards as a nucleus; provision should, however, be made to secure continuity, elasticity, and independence of political influences, and, possibly, some outside endowment with combined control would afford a more useful constitution. The closest and most cordial co-operation of the chemical profession and the industrial world must be secured and maintained, and, with this object, an advisory board representing non-official interests would be desirable. J. F. B.

New Method for Determining the Refractive Index of Liquids. A. Ledoux. (*Compt. rend.*, 1917, **164**, 305-308.)—The author has already described (*Bull. Soc.*

franç. Mineralogie, December, 1916) a method for measuring the principal refractive indices of doubly-refracting substances, based on the observation of the hindrance of a thin section placed obliquely between crossed nicols. This method suggests a simple means of measuring the refractive index of liquids. Use is made of a section, parallel to the axis of a uniaxial crystal of which the principal indices are known. By measuring the hindrance, r, of this lamina, immersed in the liquid of which the refractive index is required, under an incident angle I, the plane of incidence containing the axis, we have—

$$\mathrm{N}=\frac{n\sqrt{1-\frac{r_i^2}{r_n^2}}}{\sin \mathrm{I}},$$

r_n being the hindrance of the lamina in normal light, N the refractive index of the liquid, and n the lesser index if the crystal is positive, the greater if it is negative—that is to say, always n_o, the index of refraction for the ordinary ray. For quartz at 15° C., $n_o=1{\cdot}54425$. With a lamina of quartz parallel to the axis and 0·1 mm. thick, we have—

$$r_n=911\times10^{-6} \text{ and } \mathrm{N}=\frac{1{\cdot}54425\sqrt{1-\frac{r_i^2}{911^2}}}{\sin \mathrm{I}}.$$

If the lamina be inclined to obtain the first sensible violet, corresponding to $r_i=575$, we have $\mathrm{N}=\frac{1{\cdot}197783}{\sin \mathrm{I}}$, a formula which makes it possible to calculate the refractive index of any liquid. The paper includes a table of values of N corresponding to various values of I (for the D ray at 15° C.) from 35° to 80°. For the lower angles, readings to the nearest 1^1 give the refractive index with an error not exceeding 0·0008, whilst at the top of the scale similar readings introduce an error of less than 0·0001.

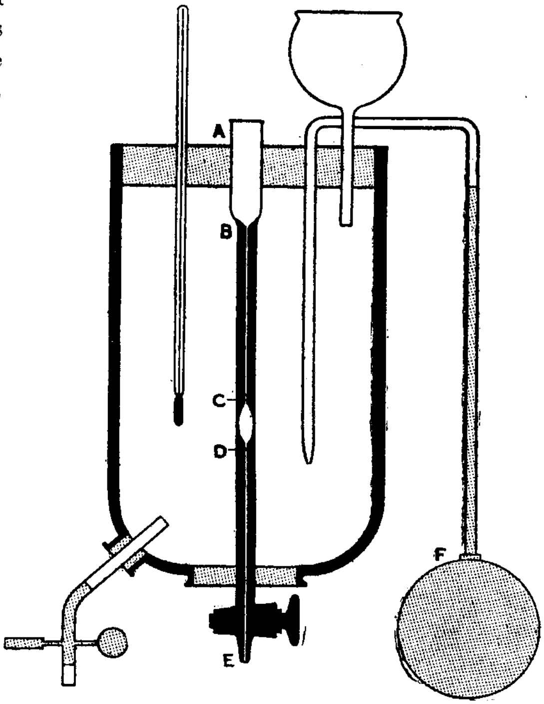
If the refractive index sought exceeds 1·55, the lamina of quartz can be inclined to obtain obscurity, in which case $r_i=0$ and $\mathrm{N}=\frac{1{\cdot}54425}{\mathrm{I}}$.

A table for use with this formula is also given, readings to 1^1 in the neighbourhood of 50° insuring determination of the refractive index within 0·0004, and in the neighbourhood of 80° within 0·0001. G. C. J.

Soluble Filters and Filtering Media. J. M. Wilkie and H. S. Anderson. (*J. Soc. Chem. Ind.*, 1917, **36,** 272-273.)—The authors describe a filter composed of a bed of coarse and fine potassium nitrate, which they found useful for filtering off potash soaps from strong alcoholic mother liquors. They wished to filter off the soaps, decompose them with aqueous acid and shake out the fats with ether. By packing the filtering medium in the cylindrical stem just above the cock of a pear-shaped separator, all the operations could be carried out in one vessel. The well-known anthracene filter is an example of another type of soluble filter, soluble in organic liquids but not in water, whilst calcium carbonate, soluble in aqueous acids but not in neutral or alkaline liquids, is a third type. A special case of the second type is that in which the medium is volatile without decomposition at moderate temperatures. Work with these other types of soluble filter is in progress.

G. C. J.

Mercurial Viscosimeter. F. M. Lidstone. (*J. Soc. Chem. Ind.*, 1917, **36,** 270-272.)—This viscosimeter was designed to work with very small quantities of oil, such as are sometimes separated in the course of analysis, but it is suggested that an instrument of the same type with larger bulb might replace with advantage the commercial instruments now in use. The bulb *BE* is a fine capillary with a small bulb blown in it. The cock is opened and clean mercury sucked up to just above *B* and the cock closed. A small measured quantity of oil (just more than sufficient to fill the bulb) is then run into the cap *AB,* where it is allowed to rest on the surface of the mercury, surrounded by the water-jacket for ten minutes to acquire the exact temperature of the water, which is kept in constant agitation by the bellows *F.* When ready to take the reading, the cock is opened and the time occupied by the mercury in falling from *C* to *D* is observed. The time reading is converted into seconds (Redwood) by the equation $R = \frac{t}{d}\kappa$, where *t* is the time of running from the new form of viscosimeter, *d* is the density of the oil at temperature of experiment, and κ a constant, readily obtained with some oil, of which a sufficient quantity is available for test in the Redwood instrument.



Consideration will show that the error due to making no allowance for variable head is negligibly small. Nor is it worth while to correct for varying time taken by the mercury itself, except in the case of very mobile oils, when, if great accuracy is required, for *t* in the above equation $t\left\{1-\left(\frac{t'}{t}\right)^3\right\}$ should be substituted, t^1 being the time taken by mercury running freely from the instrument.

The particular instrument used by the author has a capillary of 0·5 mm. diameter, a bulb of 0·18 c.c. capacity, and the diagram reproduced is drawn to scale.

It is submitted that absolute viscosities can be calculated from the time readings by the simple formula $\eta = \kappa t\left\{1-\left(\frac{t'}{t}\right)^3\right\}$, as it can be shown that the error due to variations in the density is negligibly small, and therefore the first term of Poiseuille's formula must be substantially a constant, all the other factors being invariable, whilst the second term of his formula—the so-called kinetic energy correction—is negligibly small with this instrument, owing to the relatively enormous value of *h*, due to the head of mercury. In setting up an instrument of this type, but not precisely of the dimensions shown, it must be remembered that *h* must not be increased so much that the critical speed for thin oils is overstepped and sinuous motion set up. In such circumstances, the indications of the instrument would be worthless, but the dimensions given above come well within the limits required by the formula found by Reynolds in order that a steady flow shall be produced.

G. C. J.