

THE ANALYST.

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

AN Ordinary Meeting of the Society was held on Wednesday, November 2, 1921, in the Chemical Society's Rooms, Burlington House. The President, Mr. Alfred Smetham, was in the Chair.

Certificates were read for the first time in favour of Messrs. Jack Cecil Drummond, D.Sc. (Lond.), F.I.C., Alfred William Long, John Charles Mellersh, and Charles Harold Wright, M.A. (Cantab.), F.I.C.

The following were elected Members of the Society: Messrs. James Frederick Fothergill Rowland, B.A. (Cantab.), A.I.C., and William Norman Stokoe, B.Sc. (Lond.), A.I.C.

The following papers were read: "An Improved Specific Gravity Apparatus," by C. Butler Savory, M.D., M.Ch., and "The Testing of Foodstuffs for Vitamins," by J. C. Drummond, D.Sc., F.I.C., and A. F. Watson, D.Sc., A.I.C.

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MORPHINE, CODEINE, AND NARCOTINE IN INDIAN OPIUM.

BY JITENDRA NATH RAKSHIT.

THE chemistry of Indian opium naturally differs somewhat from that of Turkish opium on account of variation in soil, climate, seeds, method of cultivation, of lancing the poppy capsules, and in the collection of opium. It would be beyond the scope of the subject to dwell more fully on the question of how the constituents of opium vary with the variations in the above conditions. It has been found, however, in the case of crops of poppy grown by Mr. G. O. B. Power, of the Government Opium Department, that healthy plants, at the first lancements of their capsules, yield opium with higher morphine content than that from weaker plants, or than the drug otherwise collected by subsequent lancements of the same capsules.

MORPHINE.—The author has been estimating morphine in no fewer than 3,000 samples of opium a year by the British Pharmacopœia and by the polarimetric methods (Rakshit, ANALYST, 1918, 43, 321), but has never met with a sample of opium which could justify the remark in "Allen's Commercial Organic Analysis" (Vol. VI., fourth edition, p. 408): "East Indian opium is, as a rule, remarkably

weak in morphine, the proportion being sometimes as low as 2.5 per cent., more commonly 3.5 and 5, and occasionally as high as 8 or 9 per cent." During this last half century there has been no such change as would produce any improvement in Indian opium in respect of its morphine content. As a matter of fact, not a single bag of opium has been received from the districts during the last seven years which gave less than 7 per cent. of morphine. The bulk of them gave 8.5 to 10.5 per cent., whilst a good quantity showed 10.5 to 12.5 per cent. Obviously, then, the former analysts must have adopted grossly erroneous methods to obtain such low results.

The British Pharmacopœia process has been well criticised by quite a number of authors, but the way in which results obtained by this process are vitiated by the tropical climate of India has not been noted to any extent. In Upper India the humidity during the summer months becomes often as low as 4 and 5, and under such conditions evaporation during the trituration in the mortar and the filtration is quite rapid, and effectively concentrates the solution. The filtered lime solution of the opium often does not amount to 51 c.c. in the case of Indian opium, as required by the B.P. process; whilst when the ether is transferred to the filter-papers, a part of it rapidly evaporates during filtration, leaving a yellowish resinous deposit of alkaloids on the top portion of the upper filter-paper, and seldom any on the counter-poised lower one. The 10 c.c. of ether recommended in the process for washing the filter-paper does not completely wash this deposit, nor does it act uniformly on the two papers. In addition to this, a small quantity of ether left on the filter-paper, after the aqueous mother liquor has passed through, always leaves a residue on the upper filter-paper only. The deposit left on the evaporation of the ether is never removed by the recommended subsequent washing with morphinated water. Such residues, however, are always found to be soluble in ether or acid.

In some laboratories methods of the United States Pharmacopœia are adopted, and since these are purely gravimetric methods, the errors due to the evaporation during the preparation of the solution and the filtration are not introduced. The prescribed washings with alcohol and ether completely remove the residue left on evaporation of the ether which escapes filtration. It must not be assumed, however, that this method is free from defects. The substance dissolved by the lime water has been taken to be pure morphine, which, however, is not the case, as is shown below. Moreover, no correction is made for the retention of morphine by the mother-liquor.

Several experiments have been made to compare the results obtained by the polarimetric process with those of the U.S.P. process, and a few typical results are given below :

Sample.	Polarimeter		Morphine	
	Result.	Per Cent.	Strength,	U.S.P.
				Per Cent.
Ghazipur	10.2	9.8
Lucknow	10.1	9.7
Cawnpore	9.8	9.6

To ascertain the amount of morphine left in solution after the precipitation of the base in the U.S.P. process, the aqueous mother liquor was thrice extracted with

ether, 100 c.c. being used each time to get rid of any codeine which might still be present in solution, evaporated to a small bulk, acidified with 1 c.c. of hydrochloric acid, made up to 100 c.c., decolorised with 20 grms. of animal charcoal, and polarised in a 200 mm. tube.

Sample.	Reading on Ventzke Scale.	Total Mor- phine in 100 c.c. gram.
1 gram. of morphine hydrochloride (dry) instead of extract from 10 grms. of opium	-1.3	0.18
Karmansa	-1.7	0.23
Ghazipur	-1.8	0.24
Gwalior	-2.6	0.36

A quantity of 0.5 gram. of morphine, obtained by the U.S.P. process, was titrated with $\frac{N}{10}$ sulphuric acid, with litmus as indicator, and the neutral or slightly acid solution was made up to 50 c.c., filtered, and polarised in a 200 mm. tube. The specific rotation was calculated by assuming the gross weight to be entirely due to morphine, and by regarding as morphine everything which neutralised acid.

Sample.	Morphine as Obtained by Titration.	Reading on Ventzke Scale.	Specific Rotation based on—	
			Gross Weight.	Titration Value.
	Per Cent.			
Ghazipur	98.34	-6.72	-116.5°	-119.5°
"	97.34	-6.80	-118.5°	-121.2°
"	96.80	-6.72	-116.5°	-120.2°
Pure morphine	—	—	-127.5°	-127.5°

Morphine (0.5 gram.), obtained by the U.S.P. process, was shaken with 50 c.c. of freshly made lime water in a 250 c.c. Erlenmeyer flask, the liquid filtered through counterpoised double filter-papers, and the residue washed with lime water until the filtrate, on acidification, ceased to give any precipitate with Mayer's reagent. The substances dissolved and undissolved by the lime water were usually determined gravimetrically. The lime-water solution was made up to 250 c.c. with lime water, and polarised in a 200 mm. tube, and the specific rotation was calculated by taking the weight of morphine to be that of the substances dissolved by lime water. The following results, however, show that the substances dissolved by the lime water are not all morphine:

Sample.	Morphine as Obtained by Solution in Lime Water.	Reading on Ventzke Scale.	Specific Rota- tion of Sub- stance Accepted as Morphine.
	Per Cent.		
Pure morphine.	100.0	-1.4°	-60.68°
Cawnpore opium	92.4	-1.2°	-56.3°
Ballia opium...	95.8	-1.2°	-53.5°

CODEINE.—Next in importance to morphine among the opium alkaloids is codeine; so its study requires some consideration. Since only very unsatisfactory determinations of its solubility were available, a fresh series of determinations has been made with all the solvents generally used for practical purposes. An excess of pure, well-powdered, dry codeine was shaken in conical flasks, at intervals, during two hours with the different solvents at different temperatures (varying not more than 2° C.), and 20 c.c. of the clear solution then withdrawn by means of a hot pipette.

SOLUBILITY OF CODEINE IN GRMS. PER 100 C.C. OF SOLUTION AT DIFFERENT TEMPERATURES.

Solvents.				20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Ether	2.5	2.8	—	—	—	—	—	—	—
Acetone	16.3	18.0	21.1	29.1	—	—	—	—	—
Chloroform	34.6	52.3	53.8	72.1	—	—	—	—	—
Benzene	7.3	9.3	15.5	23.4	38.4	58.8	63.8	—	—
Toluene	5.5	6.8	10.4	19.9	32.4	44.8	56.4	73.6	—
Alcohol	90	per cent.	V/V	22.2	34.3	50.0	—	—	—	—	—	—
"	60	"	"	20.4	48.6	59.4	65.9	—	77.0	—	84.1	—
"	50	"	"	20.0	41.9	50.6	64.7	—	75.0	—	81.4	—
"	40	"	"	19.5	26.4	40.0	51.5	—	64.0	—	78.8	—
"	30	"	"	7.8	11.6	21.6	36.0	47.1	49.2	63.7	77.4	—
"	20	"	"	3.0	3.8	7.0	11.1	18.0	26.4	47.7	61.4	—
"	10	"	"	1.5	1.8	2.4	3.1	4.1	5.2	9.9	15.8	25.0
Ammonia	10	"	W/V	0.9	1.2	1.5	1.8	2.3	2.3	3.2	—	—
"	5	"	"	1.1	1.2	1.4	1.7	2.0	2.1	2.6	—	—
"	1	"	"	1.0	1.2	1.5	1.8	2.0	2.1	2.3	2.6	3.2
Water	0.9	1.0	1.1	1.3	1.5	1.8	1.9	2.4	3.2

For the estimation of codeine in opium the method described by Andrews (ANALYST, 1911, 36, 489) has often been adopted. It is not only very lengthy, but has also several defects, more particularly when applied to Indian opium. The resinous mass which separates on the addition of sodium salicylate solution has been said to contain thebaine, but, in reality, is practically free from any alkaloid, and consists chiefly of salicylic acid and colouring matter. The results thus obtainable are hardly concordant, and the codeine isolated is seldom free from other alkaloids; the latter fact was ascertained by polarimetric examination. Codeine obtained by this process was titrated with $\frac{N}{10}$ sulphuric acid, the solution made up to 50 c.c. and polarised, and the specific rotation calculated upon the corrected weight obtained from the titration.

The figures clearly show that the codeine obtained by titration does not represent either the actual amount of codeine present or that contained in opium. Annett and Sen (ANALYST, 1920, 45, 321) have described a method for the extraction of codeine with toluene from the lime solution of opium. Attempts have been made to estimate codeine by this process in the case of twenty samples from different places, thoroughly representative of the total poppy cultivation in India, but unfortunately

in every case, the toluene emulsion could not be broken up, and hence the estimations were found to be impracticable. Moreover, the authors appear to have taken no precaution to remove porphyroxine, which is always extracted to some extent by almost all immiscible solvents from the lime solution of opium and in a moderate degree by toluene (Rakshit, *J. Chem. Soc.*, 1919, 457).

Sample.	Weight of Codeine obtained—		Specific Rotation.
	Gross.	Corrected by Titration.	
	Grm.	Grm.	
Codeine, pure	0·200	0·200	– 137·5°
Ghazipur opium	0·200	0·167	– 124·8°
Lucknow „	0·180	0·142	– 130·0°
Gwalior „	0·108	0·100	– 130·0°
Simla „	0·104	0·88	– 132·0°
Cawnpore „	0·089	0·068	– 128·0°
Azamgarh „	0·160	0·120	– 128·0°

A method for the estimation of codeine has been worked out. The opium alkaloids more or less soluble in ammonia solution which require consideration are: Morphine, pseudo-morphine, thebaine, meconidine, codamine, laudanine, laudanidine, protopine, narceine, and porphyroxine, whilst the rest may be disregarded, being thrown out of solution by ammonia. Morphine, pseudo-morphine, laudanine, and narceine, are practically insoluble in ether, and the others—viz., thebaine, meconidine, codamine, laudanine, protopine, and porphyroxine—are much less soluble in ether than codeine; but, with the exception of porphyroxine, these are only nominally present in Indian opium. Hence, the alkaloid last mentioned is the only one which would cause much difficulty if an attempt were made to isolate codeine by a method based on the above differences in properties.

An aqueous extract of opium was treated with strong ammonia (sp. gr. 0·880) and filtered, the filtrate shaken with three successive portions of ether to eliminate narcotine, the ethereal extract shaken with a 1 per cent. solution of acetic acid, and the acid solution of alkaloids separated and neutralised with calcium carbonate. When the alkaloid was re-extracted with ether by making the filtered solution alkaline with sodium hydroxide the residue, left on evaporation of the ether, did not crystallise like codeine, and, on warming with a little dilute hydrochloric acid, gave the usual red coloration of porphyroxine, which was thus proved not to have been eliminated by this process.

It was then observed that when porphyroxine was heated with dilute hydrochloric acid on a steam bath it was rapidly changed into a red colouring matter, which, when treated with caustic alkalis, gave a precipitate insoluble in ether. Codeine, under such conditions, did not undergo any change. After numerous trial experiments with this process of eliminating porphyroxine from codeine, the following scheme was ultimately found to give satisfactory results:

Twenty grms. of powdered opium and 200 c.c. of water are shaken for three

hours or more in an Erlenmeyer flask and filtered, and 100 c.c. of the filtrate are added to 20 c.c. of strong ammonia solution contained in a similar conical flask, and the mixture shaken for an hour and then filtered. One hundred c.c. of this filtrate are thrice extracted with ether in a 500 c.c. stoppered separator, 100 c.c. being used each time. The ethereal extracts are filtered into another 500 c.c. separator, and the filter-paper rinsed with 20 c.c. of ether. The extract and washings are twice shaken for ten minutes with a 10 per cent. W/V solution of hydrochloric acid, 25 c.c. being used at a time. The two acid extracts are evaporated to dryness in a basin on the steam bath. The residue thus obtained, which is generally of a dark pink colour, is dissolved in 30 c.c. of water, slightly warmed on the steam bath, the solution filtered if necessary and transferred to a separator, 50 c.c. of ether and 10 c.c. of a 10 per cent. solution of pure sodium hydroxide added, and the mixture shaken for ten minutes. The aqueous layer is transferred to another separator, and the extraction repeated twice more with similar quantities of ether. The ethereal extracts are dried over two or three lumps of calcium chloride and filtered, the separator and the filter-paper washed with 20 c.c. of ether, the filtrate and washings evaporated to dryness, the residue dissolved in 10 c.c. of $\frac{N}{10}$ sulphuric acid, and the solution titrated back with $\frac{N}{10}$ alkali with litmus indicator. The codeine present is calculated from the results, or, if suitable, the acid solution is filtered, made up to 50 c.c., and polarised in a 200 mm. tube:

$$\text{Per cent. of codeine in opium} = \frac{\text{Ventzke reading} \times 100 \times 0.3468 \times 1.2 \times 10}{-137.5 \times 2 \times 2}$$

The following are the results of the estimation of codeine in some typical samples by the above process:

Sample.	Codeine.
1. Two grms. of codeine (instead of 20 grms. of opium)	99.6 per cent.
2. Ghazipur opium	1.63 „
3. „ „ (duplicate)	1.84 „
4. Gwalior „	1.52 „
5. Lucknow „	0.88 „
6. „ „ (duplicate)	0.79 „
7. Simla „	0.89 „
8. Karmusa „	0.60 „

NARCOTINE.—Narcotine, having practically no medicinal value, has hitherto not been made the subject of much chemical investigation. Now, however, that cotarnine, one of its oxidation products, has been finding a ready market, the parent alkaloid is also receiving attention. Statements about its solubility, recorded in several places, are neither correct nor complete. Its solubility has therefore been studied in the same way as that of codeine in certain cases, and is considered to be of some practical importance.

Few methods of estimating narcotine have been described, and these are not only incomplete but decidedly erroneous. Henry ("Plant Alkaloids," p. 205) states that "narcotine is usually estimated by extracting the dried opium with dry ether or benzene, and shaking the solution with ammonia, which removes narceine. The narcotine left on distilling off the ether or benzene is dried and weighed." "Allen's

Commercial Organic Analysis" (Fourth Ed., Vol. VI., p. 401) states that "narcotine may be extracted from dried opium by ether or benzene." The narcotine thus obtained will not only contain small quantities of other alkaloids, but also the bulk of the opium wax (*cf.* Rakshit, ANALYST, 1918, 43, 321); Plugge's method (ANALYST, 1887, 12, 197) for the quantitative separation of narcotine from its hydrochloric acid solution by the addition of a concentrated solution of sodium acetate can hardly be considered as correct, as the alkaloid is appreciably soluble in the dilute acetic acid (see table above) liberated in the solution.

SOLUBILITY OF NARCOTINE IN GRMS. PER 100 C.C. OF SOLUTION AT DIFFERENT TEMPERATURES.

Solvents.			20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Acetone	4.9	6.3	7.5	9.4	—	—	—	—	—
Benzene	3.4	5.0	6.0	7.5	10.6	14.3	19.3	—	—
Toluene	2.2	2.5	4.0	4.8	7.2	9.4	12.1	17.9	20.8
Ether	0.4	0.6	—	—	—	—	—	—	—
Chloroform	45.9	48.1	50.9	53.4	—	—	—	—	—
Petroleum spirit (b.-pt. 82° C.)			0.02	0.02	0.06	0.07	0.16	0.18	—	—	—
Petroleum spirit (b.-pt. 93° C. to 127° C.)			0.01	0.05	0.09	0.13	0.15	0.21	0.29	0.51	0.64
Alcohol	100 per cent.	...	0.40	0.60	0.90	1.20	2.20	3.20	5.10	—	—
"	95	" V/V	0.45	0.65	0.97	1.70	2.10	3.30	4.60	—	—
"	90	" "	0.43	0.60	0.90	1.7	2.1	3.3	4.3	—	—
"	80	" "	0.32	0.48	0.67	1.29	1.6	2.3	4.2	—	—
"	70	" "	—	0.32	0.55	0.79	1.3	2.0	4.1	—	—
"	60	" "	—	0.22	0.29	0.49	0.74	1.35	1.8	—	—
"	50	" "	—	0.18	0.25	0.32	0.49	0.78	1.06	—	—
"	20	" "	—	0.07	0.10	0.08	0.09	0.10	0.17	—	—
Ammonia	10	" W/V	—	—	0.01	0.03	0.04	0.06	0.10	—	—
"	5	" "	—	0.05	0.02	0.04	0.04	0.04	0.04	0.05	0.05
"	1	" "	—	—	0.01	0.01	—	—	—	—	—
Acetic acid	20	" "	—	—	7.35	8.10	9.80	10.7	11.0	—	—
"	10	" "	—	—	3.10	3.5	3.9	4.0	4.0	—	—
"	5	" "	—	—	1.50	1.50	1.60	1.70	1.80	—	—
"	1	" "	—	—	0.40	0.44	0.45	0.52	0.59	—	—
Water	—	0.03	0.07	0.10	0.10	0.10	0.10	0.15	0.20

A method has been worked out and has given satisfactory results during the last four years in this laboratory: Ten grms. of dry opium powder and 5 grms. of fresh slaked lime are triturated in a mortar for half an hour and then transferred to a conical flask, the mortar being rinsed with about 10 c.c. of benzene, and the mixture is shaken well with 100 c.c. of benzene during half an hour. The clear benzene is decanted into a separator, and the residue in the flask twice more extracted with benzene, 50 c.c. being used each time. The total benzene extract is vigorously shaken with 100 c.c. of strong ammonia solution for half an hour, which results in the formation of a permanent white emulsion. This is transferred to a basin and

heated on the steam bath until the benzene has completely evaporated, leaving a soft yellowish residue on the surface of the aqueous ammonia layer. This residue is filtered off and washed until the filtrate ceases to give any odour of ammonia, and is then treated, together with the filter-paper, with 100 c.c. of 1 per cent. hydrochloric acid on the steam bath, when a pinkish solution is obtained. This acid solution is filtered into a separator, the residue washed with a small quantity of water, 100 c.c. of benzene introduced, the solution then made alkaline with ammonia and again very faintly acid with dilute acetic acid, and well shaken for ten minutes. After separation of the benzene the extraction is once more repeated, this time with 50 c.c. of benzene. The benzene extract is filtered and evaporated, and the residue dried and weighed as narcotine. The alkaloid thus obtained has been proved to be practically pure narcotine. The following are typical results of analyses by this process :

Sample.	Narcotine.
Benares opium	6·4 per cent.
Ghazipur „	3·6 „
Karmansa opium (received in 1920)	1·4 „
Gwalior „	2·8 „

The author desires to express his best thanks to Mr. F. D'Costa for analysing many samples by the above process.

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NOTES.

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

FORMULÆ FOR DILUTING ACIDS, ETC., TO A DESIRED STRENGTH.

For calculating the amount of water to be added to, say, 1 litre of nitric acid of sp. gr. 1·42 to reduce it to *e.g.*, sp. gr. 1·20, the only formula required is $W = VS$, where W represents the weight of a body or liquid with volume V and sp. gr. S . The necessary data are then obtained from sp. gr. tables.

If x represents the volume in c.c. of the diluted acid,

$$1000 \times 1.42 \times \frac{69.80}{100} = x \times 1.2 \times \frac{32.36}{100},$$

and

$$x = \frac{1420 \times 0.698}{1.2 \times 0.3236} = 2552.4 \text{ c.c.}$$

Hence, the required amount of water to be added is : $2552.4 - 1000 =$ (say) 1552 c.c. If contraction takes place during admixture the strong solution must be diluted with water, with cooling if necessary, until the required volume of liquid at 15° C. is obtained. Obviously, the above result also gives the amount of water required to dilute the strong acid to a strength of 32.36 per cent. This simple procedure, which depends on first principles only, is preferable to a formula which is not always remembered.

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THE IDENTIFICATION OF PECULIAR CONSTITUENTS OF FÆCES.

Substances alleged to have been found in fæces, when submitted for identification, call for some caution, as there is a type of patient that thinks it humorous to deceive his medical attendant and another type that malingers. In the following three cases, however, all the evidence pointed to the foreign bodies being genuine constituents of the excretions.

I. A specimen was sent with a request for information whether the creature was an intestinal parasite. It had an arch-shaped body with a tiny anterior segment and ten other segments. Along the dorsal or outer curvature the length was 1 inch, whilst the lower curvature measured $\frac{3}{4}$ -inch. The posterior segment was continued as a tail $\frac{7}{16}$ -inch long, bent at a pronounced obtuse angle at $\frac{1}{3}$ -inch from the body. It was identified as "the rat-tailed larva" of *Eristalis*, a fly of the family *Syrphidæ*, which comprises the Hover Flies or Common Drone Flies. The larvæ are said to live in liquid manure and foul water, and have been seen on watercress. Fantham, Stevens, and Theobald ("Animal Parasites of Man," 1916) only mention one specific case of human infection—that recorded by Austen—where in the autumn of 1907 a number of larvæ of *Eristalis tenax* was passed *per rectum* by a woman in Hampshire, who had recently arrived from France. The patient had eaten a considerable quantity of watercress before leaving France.

The larva was described about 1750 by Réaumur, and was called by him *le vers à queue de rat*. Henry Baker ("Of Microscopes," 1785) obtained a larva from a cistern of rain-water in August, and he observes the flies to be more common in France than in England. This author mentions the power the larva has of lengthening and retracting its tail, which he found could reach a length of four inches on occasion. This is of importance, because, until the telescopic nature of this organ is known, there is difficulty in identifying with illustrations a dead larva possessing a partly retracted tail.

The present specimen came from Kent at the beginning of October, 1921.

II. Some pale cream-coloured shreds were submitted to ascertain whether tapeworm was present. Microscopical examination indicated nothing in the contour of the fragments to suggest tapeworm, and no ova could be found. There was, instead, a matrix of some translucent substance with pieces of talc-like material embedded therein. When ignited the specimen did not emit a nitrogenous odour, but left an appreciable amount of ash containing 61 per cent. of silica, some magnesium, and traces of iron and aluminium. It also contained calcium and phosphate distinct from the magnesium silicate. Enquiry showed that the patient was in the habit of taking twenty saccharin tablets a day, which presumably formed the source of the talc, though a *post hoc* explanation of the presence of an article in fæces is unconvincing, because from time to time instances occur of masses remaining in the intestines for years before digestion.

III. This specimen consisted of five stones, each of which had a brown waxy centre and a creamy-brown powdery coating. The total weight was 1.4 grms. They had the following percentage composition: Moisture, 6.5; mineral matter, 4.0; mucin, 1.7; vegetable tissue, 2.8; resinous matter, 80.3; and other substances, 4.7. The bran of grain and a trace of cork tissue were found among the vegetable débris. No notable amounts of cholesterol, bile-pigments, or calcium carbonate were present. The extracted resin was insoluble in water, but soluble in ether, in alcohol, and in quite a small quantity of acetic acid. These results would appear to exclude euonymin and podophyllum resin, which had been prescribed, as sources of origin. Later information suggested that it might be a residue from one or other of the drugs prescribed for urinary antiseptics. A trace of iron and a faint trace of zinc, but no copper, were present.

W. PARTRIDGE.

ANALYSIS OF A SOUTH AMERICAN COPPER AXE HEAD.

Very few analyses of South American copper axe heads collected in the burial-grounds of the Indians of Peru and of Ecuador have been published. One by Humboldt indicates that the hardening of the copper making it suitable for the purpose in view was accomplished by the addition of 0.4 per cent. of tin, an addition probably of accidental origin rather than of design. A South American hatchet collected by one of us (E. K. R.), and stated to have belonged to an Inca Indian (Inca Pirqua), was submitted to analysis with the following results:

The metal possessed a coppery lustre, and was tough and malleable rather than brittle. The form of the hatchet suggested that it had been hammered into a plate and the haft burred up at the edges. It contained copper, zinc, iron, and small traces of silica, whilst tin, lead, and nickel were absent.

For the quantitative analysis the metal was dissolved in nitric acid and the copper estimated electrolytically. Iron was estimated colorimetrically in an aliquot portion of the residue and the zinc precipitated as sulphide, ignited and weighed as oxide, the method and precautions adopted by Sir W. Crookes being followed and allowance being made for the small quantities of iron. The silica was present in quantities too small for accurate estimation. Duplicate analysis yielded the following results: Copper, 96.42 and 96.45; zinc, 3.46 and 3.41; and iron, 0.09 and 0.09. Total, 99.97 and 99.95 per cent.

These results are particularly interesting in the fact that they indicate the material of the axe head to be a brass and not copper. Berthelot (*Comptes rend.*, 1893, 116, 161; 1894, 118, 764; 1897, 124, 328) found that the earlier copper articles of Chaldea and Egypt (*circa* 4000 B.C.) were made of pure copper, whilst the earlier copper-tin articles have been attributed by Coffey (*J. Anthropol. Inst.*, 1901, 31, 265) to the accidental use of a tin containing copper ore, and not to foresight on the part of the maker. Brass articles have always been considered to belong to a very late period. It may be noted that there was no reason to suspect the genuineness of the axe head in question.

A. K. GOAD AND E. K. RIDEAL.

TRINITY HALL,
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THE NATIONAL PHYSICAL LABORATORY.

REPORT FOR THE YEAR 1920.*

THE Report on the work of the National Physical Laboratory for 1920 numbers 132 pages. It comprises a Report of the Executive Council, giving a general outline of the work of all the departments, a statistical comparison of the tests made in the years ending 1914, 1919, and 1920, a statement of the work proposed for the year 1921-22 and approved by the General Board, a list of the Laboratory staff, a list of the scientific papers published by the Laboratory or communicated to scientific or technical journals, and the detailed Report of the Director for the year 1920. There is also a Report of the Advisory Committee of the William Froude National Tank, in which fifty-three ship models have been tested during the year.

PHYSICS DEPARTMENT: HEAT DIVISION.—Systematic work on the thermal conductivity and specific heat of cold storage heat-insulating materials has been carried out, and a series of reports presented to the Engineering Committee of the Food Investigation Board. Data for the thermal conductivity of all the materials commonly used for cold storage installation have been determined. The influence of baffles,

* Copies of the Report may be obtained from H.M. Stationery Office, Kingsway, London, W.C. 2. Price 5s. net.

etc., has been studied in detail, as well as the velocity and temperature distribution of the convection stream in the vicinity of a heated surface. For these measurements a convenient form of hot wire anemometer has been devised, which combines the functions of a resistance thermometer and an anemometer. Another research involved the determination of the specific heat of poor conductors, such as earth, slag, wool, cork, and charcoal. Experiments on heat loss from surfaces were undertaken for the British Portland Cement Association, and the coefficients of expansion of metals at high temperatures have been determined by means of two forms of apparatus specially devised for the purpose. During the year twenty-one Abel-Pensky flash-point apparatus have been submitted for testing.

THERMOMETRY DIVISION.—In the course of the year ending September 20, 1920, over a million and a half thermometers have been tested. The number of rejections has fallen to less than 2 per cent., the highest percentage with certain firms being 5 to 8, whilst it was over 30 per cent. in the case of a number of instruments of foreign manufacture.

RADIOLOGY DIVISION.—The primary British standard of about 30 mgrms. of hydrated radium bromide has now been supplemented by two secondary standards containing about 10 and 13.5 mgrms., which will be used ordinarily for the standardisation of quantities sent for test. Experiments on radium luminous compounds have been continued, and a research on the absorption and scattering of γ -radiation in metals is in progress.

OPTICS DIVISION.—Comparisons of different methods of refractometry have been made, and a method has been devised whereby check measurements can be made without the use of a spectrometer.

ELECTRICITY DEPARTMENT.—Much work has been done in connection with radio standards, the measurement of effective resistance at radio frequencies, etc., and various researches on valves have been continued. In addition to the testing of magnets and magnetic materials, a method has been devised for measuring the effective permeability and energy losses in thin sheet iron at radio frequencies.

PHOTOMETRY DIVISION.—Experiments have been made on ships' navigation lamps, miners' lamps, and motor-car head lights for Government Departments, and other experiments are in progress with a view to the specification of suitable lighting schemes for public buildings and offices.

METROLOGY DEPARTMENT.—Exclusive of tests of gauges for the Ministry of Munitions and of taximeters, 20,915 routine tests have been made, an increase of nearly 4,000 over the previous year. Coefficients of expansion of concrete blocks, as used in building houses, of "rustless" steel, glass, ebonite, etc., have been determined.

Physical Instruments.—In testing balances the instrument is placed $5\frac{1}{2}$ m. from the source of light and the scale on which the image is read, and the effect of radiation of heat into the balance cases has been reduced to a minimum. A set of solid rock-crystal weights (200 grms. to 1 grm.) has been obtained, and will be used as reference standards. Progress has been made in the re-verification of the Laboratory standards of mass by comparison with the Sèvres standards.

(a) *Glass Volumetric Apparatus.*—The number of vessels tested was 2,556, as compared with 1,455 in the previous year and 388 in 1917-18. During the year specifications for volumetric glassware used in milk analysis have been drawn up and approved by a conference comprising manufacturers, users, and a number of expert dairy chemists. The South African Government has agreed to recognise the National Physical Laboratory as one of the official testing stations for the volumetric glassware to be used in dairy chemistry in dairies, butter factories, etc. Most of the vessels are tested gravimetrically, and vessels which pass the test are etched with the Laboratory monogram by means of special apparatus. An investigation on the difference in volume of milk and of water delivered by pipettes under various conditions has proved valuable in drawing up specifications for milk pipettes, and has

indicated the necessity of modifying the usual type of instrument used. An investigation on the effect of varying the delivery and drainage time of pipettes of various capacities has also been completed. A volumetric method of testing butyrometers by the use of mercury has been devised.

(b) *Hydrometers*.—The number of hydrometers tested during the year was 1,481, an increase of 72 per cent. on the previous year. A detailed investigation is in progress relating to the effect of surface tension on the indication of hydrometers. New standard specific gravity hydrometers have been ordered, extending the range of the Laboratory standards from 1.85 to 2.00.

ENGINEERING DEPARTMENT.—A series of researches on lubricants and lubrication has been carried out for the Committee on Lubricants of the Department of Industrial and Scientific Research (*cf.* ANALYST, 1921, 453), and other investigations include one on the effect of pressure and temperature on the production of detonation in internal combustion engines. Various building materials, including concrete blocks, have been tested for strength, but those tested have indicated no great advance upon the usual building bricks.

DEPARTMENT OF METALLURGY.—Much work has been done in connection with light alloys, and the investigation of the constitution and physical properties of alloys of zinc containing moderate amount of copper and aluminium has been completed. Considerable progress has been made with the preparation of analytically standardised steel samples, in conjunction with a Research Committee of the Iron and Steel Institute. Samples of the millings have been sent to the co-operating analysts, and it is hoped that the standardised samples will be available for public issue in the course of a few months. The general chemistry of the Department has included analytical work on special bricks in connection with the housing schemes of the Ministry of Health.

Optical Glass Research.—The study of pot attack and the methods of producing suitable pots has been continued. Experiments on the viscosity of glass at various temperatures are in progress, and an apparatus for making such measurements at high temperatures has been devised.

Aeronautical Chemistry.—The differences between various acetates cannot at present be related to their chemical constitution, and experiments are in progress to ascertain to what extent variations in the viscosity during saponification would indicate the extent of homogeneity of the product. The study of hydrometric methods required in connection with the effects of humidity on fabrics and dopes has been continued. The Shakespear permeameter, calibrated in the Department, is now used for routine tests of the permeability of balloon fabrics by hydrogen. Experiments as to the suitability of glycerol as a standard in the viscosimetry of viscous solutions, such as dopes, have shown that commercially pure samples of glycerol exhibit considerable variation in viscosity, even when their specific gravities have been adjusted to be identical. Certain chemical tests have therefore been devised which will enable approved samples to be used by different workers so as to obtain concordant results in the examination of cellulose acetate, etc.



REPORT OF THE GOVERNMENT CHEMIST UPON THE WORK OF THE GOVERNMENT LABORATORY.*

FOR THE YEAR ENDED MARCH 31, 1921.

THE total number of samples examined during the year was 308,675, as compared with 368,898 in the preceding year, the decrease being accounted for by the diminution in the number of samples tested locally at chemical stations on the coast. The samples examined at the central laboratories in London amounted to 204,653, as against 199,388 in the previous year.

CUSTOMS AND EXCISE: Beer.—The total number of samples examined in connection with the duty on beer was 28,167, being an increase of nearly 3,000 samples. For the purpose of checking dilution and adulteration, 854 samples of beer were examined, as compared with 21 in the previous year. In 34 cases there was evidence of dilution, which in 6 cases was equivalent to the addition of over four gallons of water per barrel.

Non-Alcoholic Beers, Herb Beers, and Beer Substitutes.—Of the 61 samples of non-alcoholic beers examined, 17 contained between 2 and 5 per cent. and 1 over 5 per cent. of proof spirit. The number of samples of herb beers, ginger-beers, etc., examined was 69, of which 13 contained between 2 and 5 per cent. of proof spirit.

Imported Beer.—The importation of beer, mostly lager beer, is still insignificant, the number of samples examined being only 426, as against nearly 10,000 in the year ended March 31, 1914.

Examination of Beer and Brewing Materials for Arsenic.—The number of samples of beer, worts, and materials of all kinds tested was 1,258, of which 40 were found to contain arsenic in excess of the limits laid down by the Arsenic Commission. Of the 692 samples of malt and sugar examined only 1 contained arsenic in excess of the limit, whilst the limit was exceeded in the case of two samples out of 300 of beer and wort.

Cider and Perry.—Six samples of cider out of 79 examined were found not to consist solely of fermented apple-juice, and were accordingly charged as spirituous preparations.

Table-Water Duty.—Of the 58 mineral waters, 35 proved to be medicinal, and 23 were liable to duty. Of the 654 cordials, syrups, etc., only 19 contained more than 2 per cent. of proof spirit. Three of the 42 samples of "non-alcoholic" wines contained more than 2 per cent. of proof spirit, the highest being 3·8.

Spirits.—The declared gravity of the fermented wash was found to be understated in 41 cases out of the 395 examined.

Fusel Oil.—Fusel oil, whether imported or home produced, generally contains ethyl alcohol as an unavoidable impurity: but duty is not charged unless upwards of 15 per cent. of proof spirit is present, which was the case in 19 of the 88 samples tested.

Grogging.—In 5 cases evidence of the spirit having been extracted from the wood of the cask was obtained.

Illicitly Distilled Spirits.—Twelve suspected samples were examined, and in several instances the analytical results furnished evidence of illicit distillation. In 2 cases prosecutions were instituted and convictions obtained.

British Spirituous Preparations Exported.—During the year 22,184 samples of medicinal spirits, tinctures, perfumes, etc., were examined, to check the exporters' claims for drawback on the spirit used in their manufacture; in addition, 3,456 liniments, hair washes, etc., were tested for methylated spirit, the use of which precludes the right to drawback on exportation. Methyl alcohol was detected in one sample, and in 392 cases the alcoholic strength had been overstated.

* H.M. Stationery Office: [Cmd. 1490]. Price 3d.

Imported Spirits and Spirituous Preparations.—The number of samples of imported spirits was 2,742, an increase of about 400 samples on the previous year. Of 59 samples of methylic alcohol, 22 were found liable to duty on the ground of purity.

Duty-free Spirits, including Methylated and other Manufacturing Spirits.—The naphtha, represented by 720 samples, was approved as fit for methylating purposes, whilst 13 samples were reported as unsuitable.

Wines.—In 8 cases only was the alcoholic strength in excess of 42 degrees, probably due to overfortifying. Sherries and Marsala were usually well over 30 degrees. The total number of samples examined was 71,159, as compared with 143,544 in the preceding year, when exceptionally heavy imports of wine followed the Armistice.

Sugar, Glucose, and Saccharin.—The total samples examined number 24,334, or 32,332 including the outport chemical stations. Tests for saccharin were applied to 274 samples of imported substances.

Tobacco.—The percentage of moisture was determined in 542 samples of imported unmanufactured tobacco, whilst 10 samples were submitted for decision as to whether the tobacco was liable to duty as "leaf" or "strip." Twenty-seven samples of manufactured tobacco were submitted for classification, 12 of which contained ingredients rendering them inadmissible for importation. More than half of the 147 samples of home-grown leaf tobacco came from Methwold, Norfolk, where the experimental culture is being assisted by the Ministry of Agriculture. The percentage of moisture was determined in 6,321 samples and the oil in 457 samples of manufactured tobacco for home consumption. The samples of tobacco exported on drawback numbered 11,514, as compared with 13,797 in the previous year. Advantageous treatment in the matter of sampling is accorded to those manufacturers who furnish declarations as a basis for the payment of drawback. During the year 19,577 samples of tobacco stalks for drawback purposes, and 5,648 samples of offal snuff, shorts, and smalls, for denaturing, abandonment, the manufacture of nicotine or sheep dips, or on exportation, were examined. Seven samples of various herbal smoking mixtures were found to be free from any admixture of tobacco.

Tea.—The total number of samples examined was 32,176, which is far in excess of those received in any previous year. This is due to the importation of numerous small shipments in the form of dust or otherwise of doubtful quality. Some samples contained foreign seeds derived from grasses, which probably grew in or near certain tea-gardens. The samples reported against numbered 10,025, or 31 per cent. of those examined. The presence of the foreign substances in these was attributed to accidental admixture with small quantities of sand from the soil or to warehouse impurities. The number of samples of tea denatured with lime or asafœtida for use in the manufacture of caffeine was 749.

Coffee and Coffee Substitutes.—Of the 1,610 samples examined only one was incorrectly declared.

Cocoa and Chocolate.—The amount of raw cocoa was estimated in 6,613 samples either on importation or (for drawback) on exportation. Fixed rates, revised periodically after analysis, have been established for goods regularly imported or exported, and most of the firms engaged in the trade have taken advantage of these facilities. A method of estimating a substitute for cacao butter in chocolate has been devised in the laboratory (ANALYST, 1921, 229). Eight hundred and eighty-four samples of chocolate confectionery were found to contain spirit.

Imported Synthetic Dyestuffs.—Ninety samples of imported colours, inks, perfumes, etc., were examined to ascertain whether they contained synthetic dyes or intermediate products, the importation of which is prohibited except under licence.

Matches.—In none of the 67 samples submitted was any evidence of the presence of white phosphorus obtained.

Medicine Stamp Duty.—Seventy-eight samples were examined to establish their identity or in connection with import restrictions and the opium and cocaine regulations.

Hydrometers, Saccharometers, etc.—During the year 2,247 hydrometers, saccharometers, and graduated vessels for use at distilleries, breweries, glucose factories, and in the Surveying Department have been calibrated before being issued.

ADMIRALTY.—Samples of food on tender have been submitted for report as to conformity with specification. Other samples included ferrous and non-ferrous metals of all kinds, fuel oils, rubber washers, soaps, fabrics for sail cloths, and paints. The total number of samples was 739.

AIR MINISTRY.—Various metals and alloys have been examined, and investigations as to corrosion due to greases have been made. The number of samples dealt with was 185.

MINISTRY OF AGRICULTURE AND FISHERIES: *Imported Dairy Produce and Margarine.*—Nine samples of imported butter were satisfactory. Of 1,100 samples of margarine 19 were found to contain more than 16 per cent. of water. There was no evidence of excess of butter in any of them. All the samples of cheese were satisfactory. The fat varied from 9·3 to 39 per cent. Some of the cheese had therefore been prepared from milk from which a portion of the fat had been removed, but as there are no regulations relating to the marking of skimmed or partially skimmed cheese, no exception could be taken to the importation. Some of the samples of imported cream contained just under 9 per cent. of fat, but there was no evidence of dilution with water. Four hundred and thirty-one samples of condensed milk, including milk powders, were examined. In nine cases the condensed milk had been made from skimmed milk, but this was not indicated on the package. One of the samples was labelled “Centrifuged Separated Milk”—a description which was not considered a sufficiently clear description.

Butter and Margarine Samples taken at Factories in this Country.—The inspection in Great Britain has not been resumed since the war. Of the 155 samples from Ireland 20 contained more than 16 per cent. of water.

Sheep Dips.—Of 86 samples prepared in accordance with formulæ approved by the Ministry, 36 were rejected as being defective.

Water and Pollution of Rivers.—Twenty-four samples of river water and effluents were investigated. Two kinds of pollution appear to be extending: effluents from milk and cheese factories, and from suction gas plants using wood and sawdust fuel. The latter effluents contain products of the distillation of wood, and are toxic to fish, apart from their deoxygenating effect on well-aerated water. It has been ascertained that considerable purification of such effluents can be readily effected. Trustworthy information as to the proportions of toxic constituents in tar extracts and washings has now been obtained, and details of the methods of examination are in course of publication. In view of a recent legal decision the composition of road drainage and tars is a matter of extreme importance.

Sea Water.—An investigation as to the influence of the salinity of sea water upon fish is in progress. In order to make the results comparable with those obtained by the different countries concerned in the work, a prepared standard sea water is issued from a central bureau, and a uniform process of analysis employed. The salinity of 4,653 samples, taken at recorded depths, temperatures, geographical positions, etc., has been determined during the year.

Fertilisers and Feeding Stuffs Act.—Reports have been given on 20 fertilisers and 10 feeding stuffs in cases where there has been a discrepancy between the statement of the seller and the finding of the official analyst. In most cases the fertilisers contained less nitrogen, phosphates, or potash than the guarantee. In other cases samples sold as fish guano contained very little fish and were without appreciable fertilising value.

The feeding stuffs consisted of milling offals and various kinds of meals. In some cases there was a deficiency of oil or albuminoids compared with the guarantee on the label; in other cases foreign substances (*e.g.*, corn cockle, a poisonous weed seed, and rice husk). Some meals for feeding pigs contained nearly 8 per cent. of sand, whilst a "fish meal" consisted mainly of cereals with less than 10 per cent. of fish or meat meal. In all cases there was substantial agreement with the results of the agricultural analysts who had condemned the samples.

Miscellaneous Articles.—Two samples of exhausted raisins intended for manure contained: Water, 70.57 and 72.94; organic matter, 23.51 and 17.48; mineral matter, 5.92 and 9.58; nitrogen, 0.48 and 0.59; phosphate, 0.38 and 0.47; and potash, 0.96 and 1.40 per cent. The material was thus similar in general fertilising value to farmyard manure.

China Clay in Feeding Stuffs.—Another sample contained china clay, the addition of which to fine meals might escape detection until a chemical analysis was made. The following methods of detecting very small quantities were devised and communicated to the Ministry for circulation: (1) The fine dust passing through a sieve 100 meshes to the inch is ignited and examined microscopically with polarised light and crossed "Nicols." (2) The suspected sample is shaken with ether, and after the tube has been stood for a few minutes, the ethereal layer, which will contain the kaolin and starch in suspension, is decanted and evaporated, the residue ignited, and the ash examined microscopically. If kaolin be present the ash will consist mainly of fine crystals which show their felspathic origin.

The Composition of Oysters taken from selected ground at regular intervals during a year was determined for the Fisheries Department. In the fresh condition oyster meat contains: Water, 76 to 82; fat, 1.5 to 2.5; proteins, 9 to 12; carbohydrates, 4.5 to 8; and mineral matter, about 2 per cent. The carbohydrate matter consists mainly, if not wholly, of glycogen. The amount of glycogen estimated immediately on opening the oyster corresponds approximately with the total carbohydrates, whereas in the dried oyster meat it is only 50 to 60 per cent. of the total carbohydrates present. The dry ash-free solids contain the following proportion of food constituents: Fat, 8.5 to 11.9; proteins, 50.2 to 64.3; and carbohydrates, 22.9 to 39.4 per cent.

GEOLOGICAL SURVEY.—Fifteen samples of water from boreholes were examined. Some contained both barium chloride and sulphates, the co-existence of which in dilute brine raises interesting physico-chemical questions.

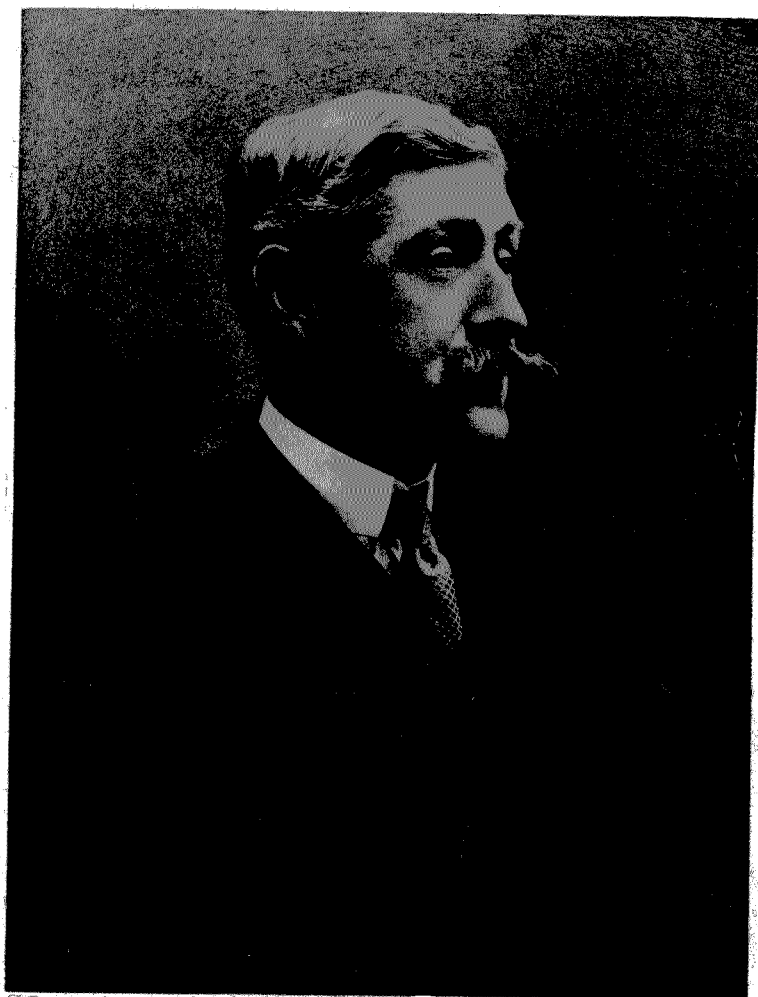
HOME OFFICE.—Ten samples have been tested for opium and certain drugs under the Dangerous Drugs Act, whilst 89 samples were examined for the police authorities. These included food mixed with phosphorus, paper saturated with petrol from premises which had been on fire, and substances found on persons alleged to be dealing illicitly in cocaine.

The examination of lead glazes, enamels, etc., affecting the health of workers in factories has been continued, and experiments were made for the Factory Department to ascertain the amount of lead and other metals discharged into the air during soldering and lead burning.

POST OFFICE.—The paper, pigments, and gum used in the manufacture of stamps were systematically examined for quality and freedom from deleterious substances. As in previous years, investigations have been made in cases of suspected fraudulent use of postage and fiscal stamps. A special inquiry was made as to the disintegrating effect of certain inks on rubber stamps, and, as the result, certain constituents of such inks were eliminated.

BOARD OF TRADE: Lime and Lemon Juice for the Mercantile Marine.—Of 228 samples of crude lime juice submitted only one was found unsatisfactory. The quantity of fortified juice approved was 25,926 gallons.

Potash Branch.—Two hundred and thirteen samples of potash from supplies



Edward Devan

from Germany were analysed. Each original sample had been divided into three parts, one of which was analysed in Germany, whilst the third was retained in a neutral country for analysis in case of dispute. There were only a few cases in which the Germans asked for the analysis of the third portion, and in each instance there was substantial agreement with the analysis here.

WAR DEPARTMENT.—The number of food samples examined was 3,249. Returned stores were also examined as to their fitness for use. The amount of tin in canned food which had been in store for a year or two was estimated in suspicious cases, and, if excessive, the foods were destroyed.

OFFICE OF WORKS, LONDON.—In addition to the examination of materials of all kinds for the public service, special investigations were made as to the suitability of paints and varnishes for protecting surfaces of metal and wood for external work. The effect of town atmosphere on building stones was demonstrated, the destructive agents being mainly sulphuric or sulphurous acids. It was also shown that ordinary domestic soot could disintegrate limestone, owing to the acid, ammonium sulphate, etc., in it. It has been established that the addition of small amounts of salt or calcium chloride to prevent freezing of the water for making cement in cold weather has no deleterious influence on the properties of the cement.

SALE OF FOOD AND DRUGS ACTS.—Thirty-six samples referred by magistrates were examined during the year, including 33 milks, 1 sausage, 1 butter, and 1 lemon squash. In 31 cases the results were in agreement with those of the analyst for the prosecution. Four of the other samples were milks in an advanced stage of butyric fermentation; with regard to these no certificate was given. The only case in which there was direct disagreement with the analyst was in connection with a sample of butter; this was alleged to contain excess water, but was found not to contain more than the legal amount. The sample of "lemon squash" contained only a small proportion of lemon constituents, the acidity being mainly due to the presence of free phosphoric acid.

Five samples were referred in cases arising from the Beer and Spirits (Prices and Description) Orders of the Food Controller.



UNITED STATES DEPARTMENT OF AGRICULTURE.

FOOD INSPECTION DECISION 182.

CITRUS FRUITS.—The following definitions and standards for grape fruit and oranges were adopted by the Joint Committee on Definitions and Standards, March 23, 1921, and were approved by the Association of American Dairy, Food, and Drug Officials, October 7, 1920, and by the Association of Official Agricultural Chemists, August 19, 1921:

Grape fruit, pomelo, is the sound, mature fruit of *Citrus grandis* Osbeck. The juice of the mature fruit contains not less than seven parts of soluble solids to each part of acid calculated as citric acid without water of crystallisation.

Orange (common, sweet, or round) is the sound, mature fruit of *Citrus sinensis* Osbeck. The juice of the mature fruit contains not less than eight parts of soluble solids to each part of acid calculated as citric acid without water of crystallisation.

The foregoing definitions and standards are adopted as a guide for the officials of this department in enforcing the Food and Drugs Act.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Chlorine in Milk without Calcination. J. Werder. (*Mitt. Lebensm. Hyg.*, 1921, **12**, 37-38; *Chem. Abstr.*, 1921, **12**, 1950.)—Fifty c.c. of the milk are boiled for thirty minutes with 25 c.c. of nitric acid (sp. gr. 1.15). After cooling, 20 c.c. of $\frac{N}{10}$ silver nitrate solution are added, and the mixture heated on a water-bath for fifteen minutes and filtered. Any fat remaining in the filtrate is extracted with 20 c.c. of ether, after which 2 c.c. of saturated ferric ammonium alum solution are added, and the excess of silver titrated with $\frac{N}{10}$ ammonium thiocyanate solution. The results quoted agree well with those obtained by the usual method.

T. J. W.

Calcium Content of White of Egg. H. Kreis and J. Studinger. (*Schweiz. Apoth. Zeit.*, 1921, **59**, 193-196; *Chem. Abstr.*, 1921, **15**, 2315.)—The statement of Rözsenyi's (*Chem. Zeit.*, 1904, 620), that the amount of calcium oxide in the ash of the whites of eggs which had been kept twenty-four hours in lime water increased from 1.83 to 2.03 per cent., is inconclusive, since the same amount may be present in untreated eggs. Should the yolk membrane break and the yolk (11.54 to 12.32 per cent. CaO in the ash) mix with the albumin higher results for the latter will naturally be obtained. The whites of eggs which had been kept for nineteen days in lime water yielded 0.8 per cent. of ash containing 1.18 per cent. of calcium oxide. In another test the fresh eggs showed 0.75 per cent. of ash, with 2.64 per cent. of calcium oxide; after one month, 0.8 per cent. (2.04 per cent. CaO); three months, 0.76 per cent. (1.44 per cent. CaO); and six months, 0.73 per cent. (CaO, 1.12 per cent.). The albumin of fresh eggs yielded ash containing 0.59 to 4.25 per cent. of calcium oxide; there was no absorption of calcium after they had been kept for months in lime water, and the specific gravity of the eggs was unaltered, but the yolk membrane was rapidly weakened. These results show that the amount of calcium in the ash of the albumin affords no proof of the preservation of the eggs in lime water.

Caviare and Caviare Substitutes. P. Buttenberg. (*Chem. Zeit.*, 1921, **45**, 1025-1026.)—During and since the war a number of preparations of the roe of salmon, cod, sole, herring, and other sea fish, has been put upon the market as "caviare," in place of the real (Russian) article, composed of the eggs of the sturgeon preserved by freezing, salt, or boric acid. (In Russia preservation other than by freezing or salting is forbidden.) The eggs of all the above fishes are distinguishable from those of the sturgeon by their smaller size; moreover, those of the sturgeon are of a characteristic dark grey or silver grey colour. It is urged that such substitutes should be compulsorily labelled with the name of the fish from which they have been prepared, and not described simply as "caviare"; also, that

artificial colouring to imitate the true caviare colour should be forbidden. Artificial colouring can easily be detected by shaking the caviare with water and alcohol; artificial dyes colour the liquid. The condition of the sample is best determined by estimating the acidity and the ammonia liberated on distillation with magnesia. The dark-coloured fish roes often show an acidity of 17 to 19 mgrms. and an ammonia content of 190 mgrms. per kilo, but there are other preparations from which the ammonia has been almost completely removed by washing with water.

H. E. C.

Impurities of Cacao. E. Wilczek. (*Schweiz. Apoth. Zeit.*, 1921, **59**, 120-126; *Chem. Abstr.*, 1921, **15**, 2315.)—An indication of the origin of cacao and of its value may be obtained from the nature of the impurities normally present. The impurities characteristic of samples from tropical America include: *Cocos* spec., *Astrocaryum* spec., *Maximiliana* spec., *Euterpe oleacea*, *Phytelephas macrocarpa*, *Bertholletia excelsa*, *Dipterix odorata*, *Vittellaria mammosa*, *Mammea americana* and *Cupuassu*. In the case of Cameroon cacao the following impurities are distinctive of the origin: *Elæis guineensis*, *Cocos nucifera*, *Amomum melaguetta* and *grandiflorum*, *Cola vera* and *acuminata*, *Arachis hypogæa*, *Voandzeia subterranea*, *Physostigma cylindrosperma*, *Pentaclethra macrophylla*, *Monodora myristica* and *angolensis*, *Xylopia* spec., and *Carapa procera*.

Estimation of Reducing Sugars in Lead-Preserved Sugar-Cane Juices. J. B. Harris. (*J. Ind. Eng. Chem.*, 1921, **13**, 925-926.)—To obtain the correct quantity of reducing sugars in samples of sugar-cane juices which have been preserved with lead acetate it is necessary to remove the lead before the sample is filtered. Oxalic acid is the best substance to use for precipitating the lead; the usual neutral salts are unsuitable for the purpose, since their use causes the results for the reducing sugars to be too low.

W. P. S.

Methods for the Analysis of Artificial Honey. A. Behre. (*Chem. Zeit.*, 1921, **45**, 1002-1003.)—The methods for estimating the total dry matter, cane sugar and starch glucose in artificial honey, are reviewed. The refractometer affords the best method for estimating the total dry matter. The process of inversion gives rise to the formation of certain condensation products, which will reduce Fehling's solution and have a specific rotation similar to that of fructose, so that the determination of sucrose and dextrose by the Fehling-Allihn or Clerget processes and by the polarimeter generally gives too high results. For this reason the iodine process is to be preferred for accurate work; but the polarimeter answers satisfactorily for approximate analysis, for which purpose the specific rotation of artificial honey should be taken as -20° . Owing to errors in the sugar estimations, the determination of the so-called sugar-free dry matter is usually quite inaccurate, and, in the present state of knowledge, cannot be made accurate. The sugar-free dry matter sometimes contains lævulinic acid and a little formic acid, and detracts from the food value of the honey. The iodimetric estimation of the sucrose is carried out as follows: Twenty c.c. of a 1 per cent. solution of the honey are diluted to 50 c.c., and 3 c.c. of hydro-

chloric acid (sp. gr. 1.19) are added; the mixture is heated quickly in a water-bath to 69° C., kept at this temperature for five minutes, and then cooled; phenolphthalein is added and 33 per cent. sodium hydroxide solution run in until the colour is pink. This colour is discharged with $\frac{N}{10}$ acid, 25 c.c. of $\frac{N}{10}$ iodine solution are added, then 29 c.c. of $\frac{N}{10}$ sodium hydroxide solution, and the mixture is allowed to stand for 20 minutes, after which time it is acidified with dilute sulphuric acid and titrated with $\frac{N}{10}$ thiosulphate solution. The sucrose is measured by the difference in iodine value before and after inversion, as above (*cf.* ANALYST, 1921, 368).

H. E. C.

Artificial "Honey." A. Beythien. (*Chem. Zeit.*, 1921, 45, 1026-1027.)—At a conference of chemists connected with the industry the following specifications were adopted: Artificial honey must possess good keeping qualities; it must not yield more than 3 per cent. of ash, must have a honey-like aroma, and may be coloured artificially. The acid used for the inversion must be technically pure, and contain no injurious substance; the free acidity left in the honey must not exceed 2 mgrm. equivalents per 100 grms. The total dry matter must be more than 78 per cent., and the content of uninverted cane sugar must be not more than 25 per cent. The addition of starch syrup and glucose is allowed to a total amount of 20 per cent. if both materials are of a quality specially fitted for human consumption. The product must give a strong reaction in Fiehe's test (ANALYST, 1909, 34, 399; *cf.* 1908, 33, 397), and the addition of some natural honey as flavouring is allowable. The package must be distinctly labelled "artificial honey."

H. E. C.

Grape-Seed Oil. F. Rabak. (*J. Ind. Eng. Chem.*, 1921, 13, 919-921.)—The variety of grapes grown for the manufacture of grape-juice in the United States is the well-known Concord grape; about 1,100 tons of grape-seeds are obtained annually, as a by-product, in the manufacture of the juice. The seeds yield about 13 per cent. of oil, which may be used for edible purposes. The refined oil has a pale yellow colour, a pleasant odour and taste, and the following physical and chemical characteristics: Sp. gr. at 25° C., 0.9204; solidifying point, -22° to -24° C.; acid value, 0.74; saponification value, 192.2; and iodine value, 135.8. These results differ in many respects from those recorded in literature for other grape-seed oils. The composition of the oil is (approximately): Linolin, 53.6; olein, 35.9; palmitin, 5.2; stearin, 2.2; and unsaponifiable matter, 1.6 per cent.

W. P. S.

Glycerides of Goose-Fat. A. Bömer. (*Chem. Zeit.*, 1921, 45, 1026.)—Goose-fat contains the glycerides of palmitic, stearic, and oleic acids, and not those of margaric acid, as is stated by Klimont and Mayer (*cf.* ANALYST, 1915, 40, 349). Solid glycerides are present in small quantity as palmitodistearin and dipalmitostearin; liquid glycerides preponderate as triolein and palmitodiolein, together with some stearodiolein.

H. E. C.

Detection of Saccharin in Wine. W. Fresenius and L. Grünhut. (*Zeitsch. anal. Chem.*, 1921, **60**, 353-359.)—The wine (500 c.c.) is evaporated to a small volume to remove the alcohol, and the residue diluted to 450 c.c. with water, acidified with 5 c.c. of dilute sulphuric acid (sp. gr. 1.11), and then extracted successively with 60 c.c. and two portions of 25 c.c. of ether. After removal of the ether, the wine is evaporated to 200 c.c., cooled, and shaken out three times with 200 c.c. of ether. The bulk of the mixed ether extractions is then distilled, and the last portion thereof evaporated in a porcelain dish. The residue is taken up with 50 c.c. of water and the mixture evaporated to dryness, this process being repeated; the residue is then dissolved in 5 c.c. of $\frac{N}{4}$ sodium hydroxide solution, the solution heated on the water-bath, and 5 per cent. potassium permanganate solution added in small quantities until the pink colour persists for one minute. The liquid is now acidified, and more permanganate added, if necessary, to retain the pink colour for a minute; a dilute solution of sulphur dioxide is next added in quantity just sufficient to decompose the excess of permanganate and dissolve any manganic oxide which may have separated out. The clear liquid is extracted three times with an equal volume of ether; the ether is distilled off, and the last portion evaporated at a low temperature in the presence of 1 c.c. of water. After complete removal of the ether, and cooling, a sweet taste indicates the presence of saccharin, which may be confirmed by evaporating the residue in a silver crucible and fusing it for half an hour at 250° C. with 0.5 gm. of sodium hydroxide. The fused mass is dissolved in water, the solution acidified with dilute sulphuric acid and extracted with ether, and the ether extract evaporated and tested for salicylic acid with ferric chloride. A violet coloration confirms the presence of saccharin.

H. E. C.

Estimation of Camphor in Camphorated Oils. D. A. Wallace and S. B. Plummer. (*Amer. J. Pharm.*, 1921, **93**, 600-604.)—The results of experiments described show that the camphor present may be estimated from the loss on heating 5 grms. of camphorated oil at 120° C. for five hours for cotton-seed oil; four hours for olive and arachis oils; and three hours for sesame oil; and allowing for the loss or gain in weight on 4 grms. of the oil without camphor by adding or subtracting for the respective oils, +0.0142, +0.0138, +0.0108, -0.0010. For example, 5 grms. of cotton-seed oil containing 20 per cent. of camphor lost 0.9855 gm. in five hours, whilst 4 grms. of the oil alone gained 0.0142 gm.; the camphor present would therefore be $0.9855 + 0.0142 = 0.9997$ gm. The saponification values of the oils were but little affected by heating at 120° C., but the iodine values were lowered and the refractive indices raised. In the second method examined the camphor was estimated polarimetrically at 20° C. in a half-shadow single-wedge compensating saccharimeter, a 200 mm. tube being used, and a 2 cm. cell of 10 per cent. dichromate solution interposed between the light and illuminating lens in order to compensate for difference in colours of the field. The calculated angular rotation for a 200 mm. tube was found to be 0.98 to 0.99 for each per cent. of camphor in the case of solutions of standard pharmacopoeial strength; the oils alone showed slight optical activity, e.g.: Cotton-seed oil, -0.45° V; arachis oil, -0.1° V; olive oil, +0.2° V; and sesamé oil, +2.85° V.

R. G. P.

New Test for Formaldehyde with Resorcinol and Sulphuric Acid
R. Cohn. (*Chem. Zeit.*, 1921, **45**, 997-998.)—The colour reactions of oxalic, formic, and tartaric acids, with resorcinol and sulphuric acid (*cf.* ANALYST, 1921, 296), are not sufficiently sensitive for the detection of these acids in preserved foodstuffs, though the reactions are not affected by acetic, lactic, succinic, citric, malic, and benzoic acids. The following test is given for formaldehyde: Two c.c. of a 1 per cent. aqueous solution of resorcinol are mixed with 2 c.c. of the liquid to be tested, and a layer of concentrated sulphuric acid is run underneath. A white flocculent precipitate, which gradually diffuses upwards, forms at the zone of contact, and under it is formed a violet-red ring. Oxalic and formic acids do not interfere, and give respectively a blue and orange ring, and if the sulphuric acid underneath is gently warmed a deep red colour is produced by tartaric acid, while the formalin white ring is not affected. The test is more sensitive than any previously described, and will detect 0.05 mgrm. of formaldehyde. The white flocculent ring is characteristic of aldehydes: formaldehyde gives a violet ring underneath, benzaldehyde gives a yellow ring, acetaldehyde a deep green, hexamine a greenish-brown, and furfuraldehyde gives a dark violet ring with a yellow layer below it.
H. E. C.

Decomposition of Atropine. **D. B. Dolt.** (*Pharm. J.*, 1921, **107**, 286-287.)—In the B.P. method of estimating alkaloids in belladonna extract, the final extraction with chloroform is made in presence of ammonia. Should only a slight excess of ammonia be added and the extraction be carried out at once, there will only be a slight loss of alkaloids, but if the solution be allowed to stand for some hours in contact with ammonia or sodium carbonate a large proportion of the alkaloids will be decomposed. For example, an extract of belladonna was diluted, acidified, and extracted with chloroform as the B.P. directs, and the acid aqueous portion divided into three parts, which were left for sixteen hours, one without addition, one with excess of sodium bicarbonate, and one with excess of ammonia. The amounts of alkaloids found in the three portions were 1.03, 0.91, and 0.52 per cent. respectively. Analogous results were obtained with solutions of pure atropine sulphate.

Salicin Content of British Columbian Willows and Poplars. **R. H. Clark and K. B. Gillie.** (*Amer. J. Pharm.*, 1921, **93**, 618-620.)—The salicin content of the barks of a number of species of *Salix* and of *Populus* was estimated by a modification of the usual method of hydrolysis with emulsin. The following average amounts were found in the spring and autumn respectively: *Salix Nuttallii*, 3.90, 4.49; *S. Hookeriana*, 0.81, 5.09; *S. sitchensis*, 2.80, 7.38; *S. lasiandra*, 2.50, 2.51; *S. purpurea*, 3.83 (autumn); *Populus trichocarpa*, 0.96, 3.86; and *P. tremuloides*, 3.77, 2.45. per cent.
R. G. P.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Occurrence of Quercetin in Brown-Husked Maize. **C. E. Sando and H. H. Bartlett.** (*J. Agric. Research*, 1921, **22**, 1-4.)—The husks of a brown-husked type of maize contain free quercetin and a glucoside which, on hydrolysis, yields quercetin and dextrose. Both compounds are lemon-yellow in colour.

Chemical Study of Certain Pacific Coast Fishes. D. B. Dill. (*J. Biol. Chem.*, 1921, **48**, 73-82.)—Analysis of the edible portion of twenty-one samples of the California mackerel (*Scomber japonica*) gave the following results: Total solids, 24.62 to 38.80; ether extract, 0.63 to 18.12; ash, 1.24 to 1.50; and nitrogen, 3.16 to 3.77 per cent. Large mackerel were usually fatter than small mackerel of the same school. Analysis of other species of mackerel-like fish are also given. The variations in the composition of mackerel during one season were not parallel to those of another season. With some exceptions, the fish showed an increasing fat content through the summer and early autumn.

Chemical Study of the California Sardine (*Sardinia cærulea*). D. B. Dill. (*J. Biol. Chem.*, 1921, **48**, 93-103.)—Tables are given showing for the different months of the year the average composition of the edible portions of Californian sardines of different sizes, namely: (1) "Quarters," weighing 15 to 40 grms. each; (2) "halves," 48 to 70 grms.; (3) "small ovals," 80 to 120 grms.; and (4) "large ovals," 140 to 260 grms. For class (4) the percentage composition varies between the limits: Solids, 21.08 to 40.30; ether extract, 0.75 to 21.38; total nitrogen, 2.79 to 3.38. In three samples the percentages of glycogen were 0.50, 0.17, and 0.22 in the edible portion. The conclusions drawn from the results obtained are as follows: Individual sardines of the same size and from the same school vary greatly in composition; the fat content is at a maximum in the summer months with small sardines, and usually increases with the size of the fish; with large sardines the fat drops from a maximum in December or earlier to a minimum in May; there is no evidence that the growth of the reproductive organs draws largely on the reserve store of fat; any dependence of the percentage of fat in the sardine on the sea temperature is a remote one.

T. H. P.

Preservation of Fish Frozen in Chilled Brine. Penetration of Salt. L. H. Almy and E. Field. (*J. Ind. Eng. Chem.*, 1921, **13**, 927-930.)—When fish (herrings, flounders, whiting, etc.) were frozen by immersion in chilled brine, the outer muscular layer, one-eighth inch in depth, absorbed from 0.32 to 6.22 per cent. of salt, calculated on the dry substance. The absorption of the salt was not affected by the concentration of the brine, or by slight alterations in the temperature of the latter. The greater part of the salt was absorbed during the first thirty minutes of the immersion period (two hours); when the fish was cooled to about 0° C. before immersion, the amount of salt absorbed increased considerably.

W. P. S.

Digestibility of Some Hydrogenated Oils. A. D. Holmes and H. J. Deuel. (*Amer. J. Physiol.*, 1921, **54**, 479-488; *Chem. Abstr.*, 1921, **15**, 2113.)—The digestibility coefficients for man of oils hydrogenated to different degrees of hardness were determined with the following results: Cotton-seed oil hydrogenated to melt at 35°, 38.6°, and 46° C., showed digestibility coefficients of 96.8, 95.5, and 94.9 per cent. respectively. In the case of hydrogenated arachis oil, melting at 37°, 39°, 43°, 50°, and 52.4° C., the respective digestibility coefficients were 98.1, 95.9, 96.6, 92.0, and 79.0 per cent. Hardened maize oil, melting at 33°, 43°, and 50° C., showed coefficients of 94.7, 95.4, and 88.5 per cent. respectively.

Examination of Proteins in Cow and Ox Serum, Colostrum, and Milk by Racemisation. H. E. Woodman. (*Biochem. J.*, 1921, **15**, 187-201.)—The identity or non-identity of proteins was determined by the following method: The total globulin was removed by half-saturation of the neutral solution with ammonium sulphate, the pseudoglobulin and euglobulin being then separated by dialysis. The albumin in the filtrate from the total globulin was precipitated by the addition of the necessary amount of $\frac{N}{5}$ sulphuric acid and an equal volume of saturated ammonium sulphate solution, and the precipitate was freed from ammonium sulphate by dialysis. The proteins were finely ground and dried for several days *in vacuo* over calcium chloride, after which 1 gm. of the dry material was transferred to a 50 c.c. flask containing a little water, gently shaken to dissolve or keep the protein in suspension, and 25 c.c. of *N*-sodium hydroxide solution, free from carbonate, were run in. The flask was filled almost to the mark with water, and placed in an incubator at 37° C., and, on reaching that temperature, the liquid was made up to the mark, mixed, and filtered into a small stoppered flask, which was kept in the incubator. The optical rotation was read in a 100 mm. tube at intervals during about three hundred hours, the reading being then practically constant. A curve was plotted from the results, the abscissæ representing the number of hours and the ordinates the values of $[\alpha]_D$ obtained. Each protein showed a distinctive curve, giving the same initial and final rotations and the same rate of diminution throughout. Further, the same optical behaviour was observed when the proportions of alkali and protein were varied. The results show that euglobulin and pseudoglobulin are identical, whether derived from serum or colostrum; the albumin of milk is identical with that of colostrum; lactalbumin and serum albumin are distinct proteins; pseudoglobulin, whether coagulated or not, yields the same results; and globulin is a definite compound, the composition of which is unaffected by different methods of preparation. T. J. W.

Substances Precipitated by Mercuric Sulphate from Hydrolysed Caseinogen and the Isolation of Tryptophane. H. Onslow. (*Biochem. J.*, 1921, **15**, 392-399.)—The following substances were isolated from the products of the hydrolysis of caseinogen with baryta by means of precipitation with mercuric sulphate, decomposition of the precipitate with hydrogen sulphide, further digestion with trypsin and erepsin, and reprecipitation of the products: Tyrosine, leucine, cystine, and other mono-amino acids, glutamic and aspartic acids, histidine and proline, but neither lysine nor arginine. Since some tyrosine remains combined after drastic acid hydrolysis of caseinogen, this amino-acid is not separated quantitatively early in digestion. By the following method a yield of 1.3 to 1.7 per cent. of tryptophane may be obtained without difficulty: One kilo of caseinogen is added gradually, with continual stirring, to a solution of 136 grms. of crystallised sodium acetate in 10 litres of tap-water. Strong sodium hydroxide solution is introduced until the suspension is alkaline to cresol red and acid to phenolphthalein, when the P_H value will be about 8.1. From 15 to 20 grms. of trypsin, 20 grms. of sodium fluoride, and 50 c.c. of toluene are then added, the mixture poured into large bottles, and placed in an incubator at a minimum temperature of 38° C. If, after three or four days, crystals of tyrosine have not formed on the sides of the bottles, more

enzyme is added, and the bottles returned to the incubator. On completion of digestion the mixture is filtered, after the addition of kieselguhr, and 13 c.c. of ice-cold 50 per cent. sulphuric acid are added to each 87 c.c. of the filtrate, followed by 120 to 150 c.c. of the mercuric sulphate reagent to every litre. The mixture is left overnight and then filtered, and the residue washed with 7 per cent. sulphuric acid until it gives a negative result with Millon's reagent. Finally, it is washed with water, then suspended in a litre of water, treated with hot 40 per cent. baryta solution until alkaline, and decomposed with hydrogen sulphide. The liquid is filtered, heated under reduced pressure to remove hydrogen sulphide, and treated with either baryta or sulphuric acid to adjust the P_H value to 8.1, when trypsin is again added and the digestion repeated during five to seven days. The resulting liquid is rendered neutral to litmus and concentrated under reduced pressure to about 170 c.c. The solution obtained is warmed to 70° C. and extracted with 10 to 15 portions of pure butyl alcohol, which is subsequently distilled under reduced pressure until tryptophane crystallises. After separation of the deposit, a second and third crop of crystals may be obtained by further concentration, until the solid is precipitated in a gummy condition. A yield of 10 to 15 grms. of tryptophane should be obtained, and it may be purified by boiling it with 60 per cent. alcohol and a little charcoal and recrystallising it. The gummy precipitate, which also contains tryptophane, may be added to a subsequent preparation before precipitation with mercuric sulphate.

T. J. W.

Action of Alkalis and of Pectase upon Pectin. F. Tutin. (*Biochem. J.*, 1921, 15, 494-497.)—Pectins prepared from apple pomace, carrots, turnips, and mangold wurzels, when purified, were immediately neutralised by 1.05 per cent. of their weight of sodium hydroxide, but after standing in the cold for half an hour in presence of excess of alkali it was found that they had taken up 12.35 per cent. of their weight of sodium hydroxide, this figure not being increased by prolonged standing. Addition of excess of acid produced a precipitate of pectic acid. In the same experiment repeated at 80° C. there was much decomposition, but there was no definite end point or precipitate of pectic acid. Where the cold mixture obtained in the first experiment was slightly acidified and fractionally distilled, acetone and methyl alcohol, in the respective proportion of 1 and 2, were the only products obtained. On treating a solution of pectin overnight with calcium carbonate and pectase (obtained by grinding clover with water), and subsequently distilling the liquid, acetone and methyl alcohol were obtained in the same proportion as by the action of alkali. The residue consisted of a gelatinous mass of calcium pectate. These results indicate that pectin probably consists of the dimethyl-isopropenyl ester of pectic acid.

T. J. W.

Supposed Importance of Vitamins in Promoting Bacterial Growth. J. W. McLeod and G. A. Wyon. (*J. Path. Bact.*, 1921, 24, 205-210; *Chem. Abstr.*, 1921, 15, 2291.)—Experiments were made with the object of utilising bacterial growth as an index of the presence of vitamins. The most striking results were obtained with a kidney extract, minute quantities of which had a stimulating action. The

growth-promoting power of fresh blood or serum did not show any definite relationship to the known vitamin content, whilst, on the other hand, charcoal, which is devoid of vitamins, had a stimulative effect. The growth-promoting power of a serum was partially destroyed by heat for the pneumococcus, but not for the meningococcus.

Seed of the Georgia Velvet Bean. B. Sure and J. W. Read. *J. Agric. Research*, 1921, 22, 5-15.)—The Georgia velvet bean, *Stizolobium deeringianum*, is being cultivated in increasing quantities in the United States, and is usually ground up, either with or without the pods, for winter fodder. Experiments upon rats have shown that the bean is injurious if used to the extent of 40 per cent. of the ration. The injurious action is to a large extent eliminated by heating the seed for an hour in an autoclave, and up to 60 per cent. may then be used in the ration. Unlike most seeds hitherto studied, this bean is very abundant in the fat-soluble vitamin, which is not destroyed after the seed has been heated for an hour under a pressure of 15 lbs. The water-soluble vitamin, however, is of low concentration in the hulled seed. Two globulins and an albumin (low in histidin) have been isolated from the bean, but both the proteins and the salts in the seed are of a deficient character for growth.

Factors Influencing the Value of Milk and Butter as Sources of Vitamin A. J. C. Drummond, K. H. Coward and A. F. Watson. (*Biochem. J.*, 1921, 15, 540-552.)—Rats whose growth had been inhibited by feeding them upon a diet deficient in vitamin A were supplied daily with 2 c.c. of milk or 0.2 gm. of butter, and, after this had been completely consumed, the ration of basal food mixture was supplied. Other groups of the animals were furnished with different quantities of milk and butter until a satisfactory rate of growth was obtained. The following deductions were made from an extensive series of experimental results: The vitamin content of butter is diminished if the food of the animal from which it is derived is deficient in vitamins. The milk obtained from different breeds of grass-fed cows varies, and there is frequently correlation between the amount of pigment stored in the body fat of the animal and the vitamin content of the milk. Colostrum possesses a higher proportion of vitamin than the later milk, an observation which should be of service in practical nutrition. Butter shows from one-third to one-half the vitamin activity of the milk from which it was derived. The loss is partly due to mechanical separation, and partly due to destruction. Storage of butter and the development of rancidity cause no diminution in the vitamin content, if oxidation, as indicated by bleaching of the natural pigment, is not allowed to occur. "Renovation" of rancid butter by blowing air through the melted material causes a rapid decrease in the vitamin content.

T. J. W.

Differential Dialysis of Vitamins. S. S. Zilva and M. Miura. (*Biochem. J.*, 1921, 15, 422-426.)—Collodion thimbles of varying degrees of permeability were prepared by immersing them in different concentrations of alcohol for twenty-four hours. Their relative permeability was ascertained by suspending them in running water, introducing various salt and dye solutions, and observing the time and degree of diffusion.

Yeast autolysed at 37° C. was used as the source of the antineuritic vitamin B, whilst the antiscorbutic vitamin C was derived from lemon juice neutralised by the addition of excess of calcium carbonate. The vitamin-containing solutions were dialysed in thimbles of different permeability, and then tested on rats and guinea pigs, which were fed on a basal diet free from the vitamin under examination. It was found that neither of the vitamins tested would pass through thimbles treated with 90 per cent. alcohol, but completely diffused through one treated with 95 per cent. alcohol in four days. These results agree with those obtained when dialysing solutions of methylene blue, neutral red, and safranine, and the deduction is drawn that these vitamins may be of a semi-colloid nature, but there is no evidence to show whether the molecules are simple or associated.

T. J. W.

The "Bachman Test" for Water-Soluble Vitamin B. W. H. Eddy and H. C. Stevenson. (*Proc. Soc. Expt. Biol. Med.*, 1919, **17**, 52-56; *Chem. Abstr.*, 1921, **11**, 1745.)—Yeast cells are sown in Nageli's solution contained in fermentation tubes, and incubated to induce gas formation. This solution consists of 10 grms. of dextrose, 1 gm. of ammonium nitrate, 0.05 gm. of calcium phosphate, 0.5 gm. of potassium hydrogen phosphate, and 0.25 gm. of magnesium sulphate in 100 c.c. of water. Gas evolution proceeds very slowly, or not at all, but on the addition of extracts containing vitamin B the production of gas is accelerated. The authors have confirmed these results, and have found that extracts of navy beans, starch, alfalfa, protozoa food mixtures, protein-free milk, human milk, whole milk, and milk containing small amounts of sodium hydroxide, stimulate gas production in different degrees. It is suggested that both the detection of vitamin B and estimation of the vitamin content may be satisfactorily achieved by further standardisation of the test.

T. J. W.

Colorimetric Estimation of Carnosine. W. M. Clifford. (*Biochem. J.*, 1921, **15**, 400-406.)—The precautions emphasised by Koessler and Hanke (*J. Biol. Chem.*, 1919, **39**, 497) with regard to mixing the solutions in the colorimeter cup are unnecessary. Since the colour developed is not proportional to the amount of carnosine present there is no linear relation between the two. The following modification of those authors' method is recommended: A weighed quantity of the finely minced tissue is extracted for one hour with a known volume of water at 90° C. The liquid is then filtered, and the residue squeezed out; from 2 to 10 c.c. of 20 per cent. metaphosphoric acid are added to the extract, and the mixture allowed to stand for two to twenty-four hours. After filtration, a definite volume is transferred to a graduated flask, rendered neutral to litmus by the addition of 10 per cent. sodium hydroxide solution, and diluted to a known volume with distilled water. Ten c.c. of 1.1 per cent. sodium carbonate solution are diluted with $2x$ c.c. of water, and 4 c.c. of Koessler and Hanke's diazobenzenesulphanilic acid reagent added. Exactly one minute later x c.c. of the extract are added, and the solution is transferred to one of the colorimeter cups adjusted to a thickness of 20 mm. On the solution developing its maximum colour intensity, which occurs about five minutes after mixing, it is compared with the Congo-red methyl orange standard employed by the previous

authors. The estimation is repeated until 20 mm. of the unknown solution matches 30 mm. of the standard, when the volume of extract taken contains 0.1 mgrm. of carnosine. Parallel estimations agree within 0.05 mm. of the colorimeter scale.

T. J. W.

Methods for the Estimation of Cholesterol and Allied Substances. J. A. Gardner and M. Williams. (*Biochem. J.*, 1921, **15**, 363-375.)—In the application of Windaus's method (*ANALYST*, 1910, **35**, 256) it is necessary, in order to obtain accurate results, to add from 1.5 to 2.5 per cent. excess of digitonin, and to make allowance for the solubility of the digitonides in alcohol. Thus the solubility of the cholesterol compound in 95 per cent. alcohol is 0.014 and 0.16 per cent. at 18° and 72° C. respectively. Coprosterol digitonide is more soluble than other members of the group, 96 per cent. alcohol dissolving 0.143, 0.24, and 0.83 per cent. at 10°, 15°, and 78° C. respectively. A very slight error is introduced by the washing with ether or petroleum spirit, but is in most cases negligible. Investigation of the colorimetric method, in which acetic anhydride and sulphuric acid are used, showed that the same volume of acid should be used throughout a series of estimations, approximately the same temperature should be maintained, and that varying amounts of acetic anhydride had little effect upon the result when this substance was in large excess. The digitonin method yields accurate results with ether extracts of tissues and with animal fluids, whilst the colorimetric method (which is applicable to smaller quantities) is satisfactory with serum and blood, but is more or less unreliable with tissue extracts, owing to variation in the colours obtained.

T. J. W.

Source of Error in the Colorimetric Estimation of Cholesterol in Tissue Fats. J. A. Gardner and F. W. Fox. (*Biochem. J.*, 1921, **15**, 376-378.)—Ether extracted from alcoholic potassium hydroxide solutions, which had been heated and then diluted with water, a small amount of a resinous substance, which on solution in chloroform and the addition of acetic anhydride and sulphuric acid produced a brown or red coloration, which on standing changed to a yellowish-green tint. Similar results were obtained with the duty-free non-methylated alcohol, supplied to laboratories, when boiled with sodium hydroxide or heated in sealed tubes to 110° C., or in which sodium had been dissolved, but the brown coloration did not in all cases become green. Unsuccessful attempts were made to purify the alcohol by heating with sodium hydroxide and subsequent distillation and by other methods. The alcohol and ether used, when evaporated to dryness without the addition of alkali did not give this reaction. Since the hydrolysis of fats for the estimation of sterols is effected by the use of alcoholic potassium hydroxide or sodium ethoxide solution, the coloration due to the above reaction is liable to vitiate results obtained when the acetic anhydride-sulphuric acid method is adopted.

T. J. W.

Estimation of Sugar in Normal Urine. S. R. Benedict and E. Osterberg. (*J. Biol. Chem.*, 1921, **48**, 51-57.)—The great labour involved in the mercuric nitrate method for estimating sugar in urine (*J. Biol. Chem.*, 1918, **34**, 195) is avoided by the following procedure: The urine is diluted to the sp. gr. 1.025 to 1.030, and 15 c.c.

mixed with about 1 gram. of bone black (see below) and the mixture occasionally shaken vigorously during five to ten minutes, and then filtered through a small dry filter. Such volume of the filtrate as contains about 0.001 gram. of sugar is measured into a large test-tube with a mark at 25 c.c., and water added, where necessary, to bring the volume to exactly 3 c.c. Exactly 1 c.c. of 0.6 per cent. picric acid solution (best prepared from dry picric acid) and 0.5 c.c. of 5 per cent. sodium hydroxide solution are added, and 5 drops of 50 per cent. aqueous acetone (prepared fresh every day or two) are dropped directly into the liquid, not on to the side of the tube, and the tube shaken gently and immediately immersed in boiling water for twelve to fifteen minutes. Similar procedure is followed with 3 c.c. of pure dextrose solution containing 0.001 gram. of the sugar, the two tubes being heated simultaneously. Colorimetric comparison of the two liquids is then made. When a 0.001 gram. standard is used, satisfactory results may be obtained with solutions containing between 0.00075 and 0.00175 gram. of sugar; if less than 0.0007 gram. of sugar is to be estimated it is preferable to use a standard solution containing 0.0005 gram. in 3 c.c., and to dilute in both cases to 12.5 instead of 25 c.c. The bone black is prepared by boiling 250 grams. of the ordinary commercial product with about 1.5 litres of hydrochloric acid (1 vol. acid and 4 vols. water) for about thirty minutes, collecting it on a large Buchner funnel, washing it with hot water until the washings are neutral to litmus, drying, and powdering it. For clinical purposes the use of bone black may be omitted, the resultant figures being then about 0.03 to 0.04 per cent. too high. The new method yields results which are slightly lower than those given by the mercuric nitrate method. T. H. P.

Rapid Method for the Estimation of Hippuric Acid in Urine. F. B. Kingsbury and W. W. Swanson. (*J. Biol. Chem.*, 1921, 48, 13-20.)—Fifty c.c. of the urine are boiled in a 500 to 800 c.c. Kjeldahl flask with 7.5 grams. of sodium hydroxide and 0.5 gram. of magnesium oxide, so that the volume is reduced to about 25 c.c. in 30 minutes. To the boiling liquid 1 c.c. of 7 per cent. potassium permanganate solution (approximately saturated at room temperature) is added, any left on the neck being washed down with as little water as possible. The flask is twirled gently for a minute or two, cooled under the tap, and fitted with a fairly tight test-tube condenser, down the outside of which 30 c.c. of concentrated nitric acid are slowly poured. The mixture, which is cleared by the acid, is now gently boiled for thirty minutes, or, if a lighter extract easier to titrate is desired, for forty-five minutes, with a good flow of water through the condenser, the flask being afterwards cooled under the tap, the condenser rinsed down with 25 c.c. of water to remove any benzoic acid sublimed on the bottom of the condenser, and the contents of the flask transferred to a 500 c.c. separating funnel containing 25 grams. of solid ammonium sulphate; the flask is rinsed with 20 c.c. of water into the funnel. When the ammonium sulphate is dissolved, the benzoic acid is extracted successively with 50, 35, 25, and 25 c.c. portions of neutral, well-washed chloroform, the first two portions being used to rinse the Kjeldahl flask. The combined extracts are washed in a second separating funnel with 100 c.c. of a solution of 1 c.c. of concentrated hydrochloric acid in 2 litres of saturated sodium chloride solution and drawn off through a dry filter-paper into a dry Erlenmeyer flask. The separating funnel from which

the extract has been drawn is rinsed with 20 c.c. of chloroform, this being transferred to a small beaker containing the wet filter-paper, which is then rinsed with the chloroform, the latter being poured through a dry filter into the Erlenmeyer flask containing the bulk of the extract. This is then titrated in presence of 4 drops of a 1 per cent. solution of phenolphthalein in absolute alcohol, with $\frac{N}{10}$ sodium ethoxide solution (*cf.* Folin and Flanders, *J. Biol. Chem.*, 1912, 11, 257) until a faint but distinct pink coloration is obtained. When, as in the case of nephritic urine, protein is present, the urine is collected in about 15 c.c. of 2 per cent. nitric acid. Fifty c.c. of the urine, treated with 3 or 4 drops of 0.1 per cent. solution of methyl red in alcohol, are rendered just distinctly yellow by the addition of approximately *N*-sodium hydroxide solution. The liquid is then boiled and, while boiling, is treated with sufficient $\frac{N}{10}$ hydrochloric acid to give it the first definite red colour. This procedure removes the albumin almost quantitatively, so that the subsequent titration is not affected. The coagulum of albumin on the filter-paper is washed twice with 50 c.c. of boiling water, the combined filtrate and washings being rendered slightly alkaline to methyl red, and evaporated rapidly in an 800 c.c. Kjeldahl flask over a naked flame, any bumping or frothing being checked by adding a glass bead and a drop of capryl alcohol. By supporting the funnel in the neck of the flask by means of a slice of a large cork the filtration and evaporation may be effected simultaneously. When the volume of the liquid has been reduced to about 50 c.c., 7.5 grms. of sodium hydroxide and 0.5 gm. of magnesium oxide are added and the procedure described above then followed. The method requires about two hours or, with albuminous urine, about three hours, and gives results agreeing well with those obtained by the longer Folin and Flanders' method.

T. H. P.

Estimation of Creatinine in the Presence of Acetone and Diacetic Acid.

N. F. Blau. (*J. Biol. Chem.*, 1921, 43, 105-118.)—Conflicting statements have been published regarding the effects of acetone and acetoacetic acid on the colorimetric estimation of creatinine in urine by means of alkaline picrate. The author finds that the coloration obtained is lessened in intensity by acetone in large proportion, and that the upper limit of permissible acetone may be set at 0.5 per cent.; with no amount of acetone was deepening of the colour produced. In small proportions ethyl acetoacetate lessens, and in larger proportions enhances, the intensity of the coloration, the position of the line of demarcation being difficult to establish. Acetoacetic acid, even in small amount, has a marked influence on the result, and the following method has now been elaborated for the preliminary removal of this acid from urine. If the urine is alkaline, it is treated with concentrated hydrochloric acid until its reaction is that of weak organic acids—that is, red to litmus, but not blue to Congo-red. Ten c.c. of the urine and 5 volumes of methyl alcohol are introduced into a 300 c.c. Erlenmeyer or round-bottomed flask containing a few glass beads, and the mixture slowly boiled over an asbestos mat until one to two minutes after the temperature has risen to 100° C. (In this operation, which should occupy not less than fifteen minutes, the methyl alcohol may be distilled through a condenser, the recovered alcohol being readily purified by heating in a reflux apparatus with mercuric sulphate, filtering, and fractionally distilling the filtrate.) The flask is

thoroughly cooled in running water, its contents then being mixed with 15 c.c. of saturated picric acid solution and 5 c.c. of 10 per cent. sodium hydroxide solution, and, after the lapse of eight minutes, washed quantitatively into a 500 c.c. flask, diluted to the mark, and the coloration read. This method is found to give accurate results.

T. H. P.

WATER ANALYSIS.

Fluorescein as an Aid to Tracing Underground Water. H. Stabler. (*Eng. News-Record*, 1921, 86, 639-640; *Chem. Abstr.*, 1921, 12, 1956.)—A solution of fluorescein containing 1 part in 40,000,000 is recognised by the naked eye, but practical experience has shown that the quantity used should be calculated to produce about 1 part in 10,000,000. Successful use has been made of this method in tracing underground connections, detecting leakages in canals, etc.

T. J. W.

Estimation of Phosphates in Water. D. Florentin. (*Ann. Chim. anal.*, 1921, 3, 295-296.)—Denigès' test (*ANALYST*, 1921, 24) for phosphates or arsenates is modified so as to furnish a colorimetric method for the estimation of phosphates in water: Ten c.c. of the water are treated with 3 to 4 drops of an acid solution of ammonium molybdate (100 c.c. of 10 per cent. ammonium molybdate, 300 c.c. of 50 per cent. [by weight] sulphuric acid) and then with 1 to 4 drops of stannous chloride solution (0.1 gm. of tin per 10 c.c.). In the presence of phosphates a blue colour appears in a few seconds, becomes more intense, and is constant after ten minutes: 0.01 mgrm. P_2O_5 per litre can thus be detected. The colour obtained is compared with those of standards prepared with known amounts of phosphate, but, as such standards are not stable, permanent standards prepared from indigo-carmin are convenient. Silicates also produce a blue coloration in this test, but as 0.1 gm. of sodium silicate per litre gave no appreciable colour, silicates likely to be present in water would have no serious influence.

R. G. P.

AGRICULTURAL ANALYSIS.

Method of Measuring Soil Toxicity, Acidity, and Basicity. R. H. Carr. (*J. Ind. Eng. Chem.*, 1921, 13, 931-933.)—In an acid soil a portion of the iron and aluminium is present in a readily soluble form, and can be extracted by salt solutions which are nearly neutral; if potassium thiocyanate be used, the coloured ferric thiocyanate solution is decolorised by the addition of a base, the change occurring at a hydrogen ion concentration of $P_H = 5.5$. Fifty grms. of the soil are shaken in a stoppered cylinder with 30 c.c. of a saturated solution of potassium thiocyanate in 95 per cent. alcohol (adjusted to $P_H = 5.3$). If the liquid is pink after the soil has settled, $\frac{N}{10}$ alcoholic potassium hydroxide solution is added until the pink coloration disappears. The mixture is then placed aside overnight and again titrated, if necessary. Each c.c. of $\frac{N}{10}$ alkali solution used is equivalent to 200 lbs. of calcium carbonate per acre. In cases where the pink colour does not appear when the soil is shaken with thiocyanate solution, the mixture is titrated with $\frac{N}{10}$ alcoholic hydrochloric acid solution; the calcium carbonate equivalent is calculated from the

amount of acid used. The relative amount of aluminium in solution is indicated by the depth of the blue coloration obtained when the potassium thiocyanate extract of the soil is treated with a few drops of logwood tincture. Estimation of the quantity of soluble iron and aluminium compounds is helpful in pointing to a source of some of the plant disease troubles.

W. P. S.

ORGANIC ANALYSIS.

Estimation of Alcohols and Phenols in Essential Oils by Esterification with Pyridine. H. W. van Urk. (*Pharm. Weekblad*, 1921, **58**, 1265-1269.)—In the method of Verley and Bolsing (*ANALYST*, 1902, **27**, 60) the alcohol is heated on the water-bath with excess of a solution of acetic anhydride in pyridine, water added to the cooled mixture, and the uncombined acetic acid titrated. A systematic examination of this method under varying conditions with santal wood, peppermint, and clove oils has shown that the results obtained by the addition of 50 c.c. of the reagent are higher than with the specified 25 c.c., although still too low. For example, the amount of menthol in a peppermint oil ranged from 34.5 to 40.6 per cent.; that of santalol in santal-wood oil from 87.76 to 91 per cent. (92.3 by Thoms' method); and that of eugenol in clove oil from 71.6 to 72.8 (74.8 per cent. by Thoms' method). Hence the method is only suitable for the approximate analysis of the two latter oils, and is unsuitable for peppermint oil.

Estimation of Aceto-acetic Ester. H. Yanagisawa and M. Kamio. (*J. Pharm. Soc., Japan*, 1921, 240-246; *Chem. Abstr.*, 1921, **15**, 2261.)—Ten grms. of the sample are dissolved in 100 c.c. of dilute alcohol, and 5 c.c. of the solution are treated with 50 c.c. of an aqueous solution of recrystallised sodium sulphite (25 grms. in 100 c.c.), and titrated with *N*-sulphuric acid with phenolphthalein as indicator. A separate estimation of the free acid present is made by diluting 5 c.c. of the solution with 20 c.c. of water and titrating it with standard alkali, and also of the amount of standard sulphuric acid required to give an acid reaction with 50 c.c. of the sulphite solution, and corrections are applied to the results of the first titration. The method, which is not applicable in the presence of any other aldehyde or ketone, depends upon the fact that 3 mols. of aceto-acetic ester react with sodium sulphite, liberating 2 mols. of sodium hydroxide.

Volumetric Estimation of Phenylhydrazine and its Application to the Estimation of Pentosans and Pentoses. A. R. Ling and D. R. Nanji. (*Biochem. J.*, 1921, **15**, 466-468.)—The addition of four or more equivalents of iodine to one of phenylhydrazine produces iodobenzene, hydriodic acid and nitrogen. Upon this reaction the authors base the following method of estimating pentosans and pentoses. A known weight of the substance is distilled with 12 per cent. hydrochloric acid until the distillate ceases to yield a pink colour with aniline acetate paper, when the whole distillate is diluted to 250 c.c. Twenty-five c.c. of this solution are titrated with 3-*N* sodium hydroxide solution in a 100 c.c. flask until neutral to methyl orange, an increase of temperature being avoided. The solution is slightly acidified with acetic acid, treated with 10 c.c. of an approximately 2 per cent.

aqueous solution of phenylhydrazine, diluted with water to reach the neck of the flask, which is then closed with a cork and heated for 20 minutes at 50° to 55° C. On cooling, the solution is diluted to 100 c.c. and filtered through a hardened filter-paper. Ten c.c. of the filtrate are run into 10 c.c. of $\frac{N}{10}$ iodine solution, and the mixture diluted to about 100 c.c., and titrated with $\frac{N}{20}$ sodium thiosulphate solution. A similar estimation is made with the original phenylhydrazine solution, and the difference between the amounts of sodium thiosulphate required in the two estimations is equivalent to the furfural present. The results quoted for arabinose agree well with those given by the phloroglucinol method. Sulphuric acid cannot be used in place of hydrochloric acid for the furfural distillation; when an equivalent strength of the former was used and the distillation extended over eight hours, only 85 per cent. of the possible furfural was obtained.

T. J. W.

Action of Anhydrous Stannic Chloride on Petroleum and Petroleum Distillates. G. Torossian. (*J. Ind. Eng. Chem.*, 1921, 13, 903-904.)—When anhydrous stannic chloride is added to crude petroleum or any of its distillates, a precipitate is formed immediately; the quantity, colour, and characteristics of the precipitate depend on the nature of the petroleum. The precipitate is separated readily by filtration, and, if an excess of stannic chloride has been used, the filtrate does not yield any further quantity of precipitate when more of the reagent is added. The stannic chloride reacts primarily with oxygenated bituminous substances, sulphur compounds, unsaturated organic acids and terpenes present in crude petroleum. The treatment decreases the colour of the petroleum product, but a subsequent treatment with an alkali solution is required to remove acidity, since stannic chloride does not eliminate the naphthenic acids completely.

W. P. S.

Effect of Variation in the Analytical Constants of Linseed Oil and Soya Bean Oil on the Estimation of these Oils by Means of the Hexabromide and Iodine Values. E. A. Tschudy. (*J. Ind. Eng. Chem.*, 1921, 13, 941-943.)—The hexabromide method gives results differing by +7 to -3 per cent. from the actual amount of linseed oil in mixtures of linseed oil and soya bean oil containing oils having the widest range of analytical constants, when average constants are used as a basis for the calculation; including the experimental error of the hexabromide method, the results obtained may differ by +13 to -9 per cent. from the true figure. If the amount of linseed oil in such a mixture be calculated from the iodine value, the result may differ by +16 to -17 per cent. from the quantity actually present.

W. P. S.

Need of a New Table for Specific Gravity and Percentage of Glycerol. L. W. Bosart. (*J. Ind. Eng. Chem.*, 1921, 13, 944-945.)—Gerlach's table, showing the percentage of glycerol corresponding with specific gravities at 15° C. is the most accurate one yet published, and is trustworthy, especially at the higher concentrations; his table of specific gravities at 20° C. is, however, inaccurate, and should be discarded. It is very desirable that new tables should be prepared, showing the specific gravities of glycerol solutions at 15.5° C. and 25° C.; until this is done the

following rule may be adopted: For 15° C. use Gerlach's table for that temperature; for 15.5° C., deduct 0.0002 from the specific gravity shown in Gerlach's table for 15° C., and for 25° C. use Gerlach's table for 20° C.

W. P. S.

Rapid Method for the Estimation of Fermentation Glycerol. K. Fleischer. (*Zeitsch. anal. Chem.*, 1921, 60, 330-338.)—The oxidation and the iodimetric methods being unsuitable for the estimation of the glycerol in the liquor from the sugar fermentation process of manufacture, the following rapid method of fractional distillation under reduced pressure has been perfected. A steam generator is connected, through a spiral copper superheater (with a thermometer) with a litre Classen flask fitted with a dropping funnel; the flask stands in a hot-air bath, and its side tube is connected with a round-bottomed flask in a water-bath. Into the latter flask passes a capillary tube, through which tiny bubbles of air are slowly admitted, and with it is connected a reflux condenser in which circulates warm water from the water-bath. The top of the reflux condenser is connected with an ordinary cold water Liebig condenser, to the receiver of which is attached the vacuum pump. For the estimation, steam superheated to 150° C. is introduced, 100 c.c. of the liquor are slowly dropped in from the funnel, and the air-bath gradually heated to 250° C. The water-bath is maintained at 70° C., and the pressure at 15 to 20 mm. When all the glycerol has distilled into the round-bottomed flask the steam supply is cut off, and the flame removed from under the air-bath; then the temperature of the water-bath is raised to the boiling-point, and the circulating water in the reflux condenser is also heated nearly to 100° C. The estimation is completed when there is no further distillation of water from the glycerol in the round flask. The glycerol is then weighed and its density determined by means of a pycnometer, from which data the percentage in the liquor is calculated. There is a constant small error, which, for the apparatus described, was found to be 1 per cent.; this figure is therefore added to the quantity found by experiment, and the result so obtained is within about 1 per cent. of the truth.

H. E. C.

Colour Reaction of Glycine Anhydride and of its Dipeptide Compounds. T. Sasaki. (*Biochem. Zeitsch.*, 1921, 114, 63-66; *Chem. Abstr.*, 1921, 12, 1914.)—These compounds yield red colorations with picric acid and sodium carbonate, similar to that produced by the Jaffé reaction for creatinine, but less intense. The reaction is not due to the presence of nitrogen in the molecule, since a similar coloration is produced by sugars. The author considers the active constituent to be a labile hydrogen atom, but is unable to decide upon which configuration of the molecule the colour development depends.

T. J. W.

Estimation of Sulphide, Sulphate, and Organic Sulphur in Coal. Alfred R. Powell. (*Techn. Paper 254, U.S. Bureau of Mines*, 1921, pp. 21.)—Test analyses carried out on various kinds of coals proved that Powell and Parr's method (*Bull.* 111, Eng. Experimental Station, University of Illinois, 1919, 10-35) gives accurate results. The air-dried coal is crushed to pass a 100-mesh screen. *Sulphate sulphur*.—Five grms. are digested at 60° C. for forty hours with 300 c.c. of 3 per cent.

hydrochloric acid, the filtered liquid boiled with a little bromine water and treated with ammonia. The iron in the precipitate is estimated volumetrically, and the sulphur trioxide in the filtrate as barium sulphate. *Sulphide sulphur*.—One gm. is digested at ordinary temperature for twenty-four hours with 80 c.c. of nitric acid (1 : 3 water; sp. gr. 1.12), with occasional stirring. The filtered liquid is evaporated to dryness with 2 c.c. of strong hydrochloric acid on a water-bath, the residue dissolved in dilute hydrochloric acid, and the solution poured into excess of hot dilute ammonia solution. The iron in the precipitate and the sulphur trioxide in the filtrate are estimated as before. The amount of sulphur thus found, less that of the sulphate sulphur, gives the percentage of pyritic sulphur; similarly, the iron present in pyrites is found by subtracting the first from the second iron figure. The pyritic sulphur, as calculated from the iron figure, should agree closely with the percentage found by assay. It is even recommended, for commercial work, to calculate the pyritic sulphur from the pyritic iron value, because the estimation is quicker and more accurate, and dilute nitric acid will dissolve small amounts of organic sulphur from certain coals. *Organic sulphur*.—In commercial work this is taken as the difference between the total sulphur (estimated by Eschka's method) and the sulphur present as sulphide and sulphate. The organic sulphur is present in two forms—viz., phenol-soluble and humus-sulphur. *Phenol-soluble sulphur* is estimated by digesting 1 gm. of coal for twenty hours at 150° C., under a reflux condenser with 25 c.c. of pure phenol, filtering while hot through a Gooch crucible, transferring the whole of the residue to the crucible with alcohol, and washing until the alcohol becomes colourless. The residue is washed with ether, dried in an oven, and ground up, together with the asbestos mat, with two parts of Eschka mixture; the mixture is ignited and the estimation finished as usual; the amount found, subtracted from the total sulphur, gives phenol-soluble sulphur. The *total organic sulphur* may be estimated directly by digesting the residue from the dilute nitric acid extraction, together with the filter-paper, with strong nitric acid on a water-bath until the acid has evaporated. With semi-bituminous coals, the acid treatment should be repeated several times. The dry residue is stirred up with 25 c.c. of strong ammonia and the liquid diluted and filtered. The filtrate is evaporated to dryness on a water-bath, and the residue ground up with Eschka mixture, etc., as usual. W. R. S.

INORGANIC ANALYSIS.

Methyl Orange as an Indicator in Presence of Indigo Carmine. F. X. Moerk. (*Amer. J. Pharm.*, 1921, 93, 675-679.)—A mixture of methyl orange and indigo carmine furnishes a more sensitive indication of the end point in many acid and alkali titrations than methyl orange alone, and particularly in the titration of yellow-coloured solutions (Luther, *Chem. Zeit.*, 1907, 960). The author recommends the use of an indicator composed of methyl orange 1.0 gm., indigo carmine 2.5-3.0 grms., water 1 litre. Two portions of 0.2 c.c. of this solution are each diluted with 100 c.c. of water, and to the green or greenish-yellow solution sufficient $\frac{N}{10}$ acid is added to produce a "neutral tint"—i.e., to discharge the yellow or green colour without producing a red or violet colour. One portion is reserved as a

standard, and the substance to be tested is added to the other portion, which will turn violet or purplish with acids, and yellow or green with alkalis; this liquid is then titrated with standard acid or alkali until the colour matches the standard "neutral tint."

R. G. P.

Preparation of Standard Alkali Solutions Free from Carbonate. I. M. Kolthoff. (*Pharm. Weekblad*, 1921, 58, 1413-1419).—A simple method of preparing sodium hydroxide solutions free from carbonate has been based on the observations of Anselme (*Bull. Soc. Chim.*, 1875, 24, 192), that the solubility of calcium oxide in $\frac{N}{2}$ sodium hydroxide solution at 20° C. is 20 mgrms. per litre, as compared with a solubility of 1,170 mgrms. in pure water. A litre of a 1.1 *N*-solution of commercial sodium hydroxide is shaken repeatedly with 50 c.c. of milk of lime, the mixture allowed to stand for at least a day, and the clear liquid drawn off, with precautions to prevent contact with atmospheric carbon dioxide. When diluted to $\frac{N}{10}$ strength the solution will contain, at most, 1 to 2 mgrms. of calcium per litre.

Use of Sodium Persulphate in Analysis. L. Débourdeaux. (*Bull. Sci. pharmacol.*, 1921, 28, 145-155, 191-192; *Chem. Abstr.*, 1921, 15, 2047, 2260).—Finely divided silver is converted by sodium persulphate in acid solution into a compound described as "silver peroxide." This compound is immediately reduced in the presence of oxidisable substances and is then reoxidised, and this transference of oxygen continues until the reaction is complete, this being indicated by a permanent brown coloration attributed to the silver peroxide. This latter compound, however, continues its action so long as any sodium persulphate is present. The stability of the persulphate with respect to changes of temperature is greater in non-catalysed alkaline solutions than in the preceding case, and the reaction is complete when the solution is colourless; it then shows no charring on evaporation and calcination of the residue, and does not reduce potassium permanganate. The analysis of complex compounds not readily oxidisable by the usual means may be effected by successive oxidation in non-catalysed alkaline solution and in silver-catalysed acid solution. Sodium persulphate may be used for the estimation of carbon in the following classes of compounds: (1) Compounds—*e.g.*, acetic or oxalic acids, which yield carbon dioxide when treated with the reagent in acid solution; (2) those which are completely oxidised in an alkaline solution of the persulphate—*e.g.*, cacodylic acid; (3) compounds soluble in water and acids, but which, on combustion, yield incompletely oxidised products—*e.g.*, lactic acid; (4) compounds yielding insoluble products—*e.g.*, acetyl-salicylic acid; and (5) compounds insoluble in acid, but soluble in alkaline solutions—*e.g.*, terpin, camphoric acid, etc.

Estimation of Minute Amounts of Bromine. E. Oppenheimer. (*Arch. Exp. Path. Pharm.*, 1921, 89, 17-28; *Chem. Abstr.*, 1921, 15, 2045).—A standardised chlorine solution, prepared from chloride of lime, is added in increasing quantities, in the presence of magenta and sulphuric acid, to the unknown solution and to solutions containing definite amounts of bromine. Bromo-fuchsin is formed by the

liberated bromine, and the amount of the latter is estimated colorimetrically by comparison of the changes of colour from violet and yellow.

Estimation of Sulphur Dioxide and Trioxide in Sulphur Burner Gases.

R. Dieckmann. (*Papierfabr.*, 1921, 19, 285-287; *Chem. Abstr.*, 1921, 15, 2261).—The method depends upon the use of methyl orange and phenolphthaleïn as joint indicators. The gases are passed into an Orsat apparatus, and the first change of colour, from red to yellow, gives the volume of both sulphur dioxide and trioxide; the passage of the gas is then continued until the sodium hydroxide is neutralised, and the difference between the two readings gives the amount of sulphur dioxide.

Estimation of Nitrous Fumes in Air. J. Moir.

(*J. S. African Assoc. Anal. Chem.*, 1921, 4, 3-7; *Chem. Abstr.*, 1921, 15, 2044).—A new test for nitrites or nitrous acid is described, which is similar to that of Ilosvay, but in which *p*-nitroaniline and α -naphthol are used instead of sulphanilic acid and naphthylamine. Two solutions are required: (*a*) consists of a solution of 1.5 grms. of *p*-nitroaniline in 40 c.c. of hydrochloric acid, diluted to 500 c.c.; (*b*) contains 2 grms. α -naphthol, 1.1 gm. of sodium hydroxide, and 10 grms. of sodium acetate per 500 c.c. The liquid to be tested for traces of nitrite is mixed with 1 to 10 c.c. of (*a*), heated to 50° C. until diazotisation is complete, after which solution (*b*) is added in the same quantity as (*a*). In the presence of a nitrite an orange-red precipitate of *p*-nitrobenzeneazo- α -naphthol is quantitatively obtained. It is collected, after an hour, in a Gooch crucible, dried, and weighed, 293 parts being equivalent to 92 parts of NO₂ or 69 parts of NaNO₂. The dyestuff dissolves in sodium hydroxide solution, producing an intense bluish-violet coloration, which may be used for a colorimetric estimation. *Fuse Igniter Fumes.*—According to the British Government requirement the fumes from 100 grms. of fuse must not contain more than 0.5 gm. of nitrogen peroxide. To distinguish between this compound and nitrite in smoke use is made of the acidity of the former. The following methods have given satisfactory results: (1) The gas is kept in contact with neutral hydrogen peroxide solution for twenty-four hours, and the solution then titrated with $\frac{N}{10}$ sodium hydroxide solution, with methyl orange as indicator ($\text{NO}_2 + \text{H}_2\text{O}_2 = 2\text{HNO}_3$). It was found as an empirical factor that 1 c.c. of the standard alkali = 0.0060 gm. NO₂. (2) The fumes are treated with a solution of potassium iodide (1 gm. in 20 c.c.) for at least six hours with occasional shaking, during which the walls of the container should be thoroughly wetted, and the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate solution. One c.c. of the latter is equivalent to 0.0051 gm. of nitrogen peroxide, instead of the theoretical value.

New Method for the Estimation of Arsenic. J. Cribier.

(*J. Pharm. Chim.*, 1921, [vii], 24, 241-246).—The yellow coloration produced by hydrogen arsenide on mercuric chloride paper is converted into deep brown when the paper is immersed in 10 per cent. potassium iodide solution, and after the paper has been washed and dried this coloration exhibits great stability towards light and moisture. The yellow or grey colorations produced by hydrogen sulphide, phosphide,

or arsenide with mercuric chloride are also fixed by potassium iodide, but the original colour is not changed. Further, compounds capable of yielding hydrogen sulphide or phosphide, when reduced by means of zinc and sulphuric acid, may be instantly oxidised to sulphate or phosphate by a few drops of potassium permanganate solution, the excess of which may then be destroyed by addition of a trace of hydrogen peroxide. The manganous sulphate in the solution is without influence, arsenic in any form being liberated as hydrogen arsenide. The apparatus used consists of an ordinary wide-mouthed 120 to 150 c.c. flask closed by a cork traversed by a glass tube, 5 to 5.5 mm. in bore, and drawn out at its lower end to a narrow orifice; at 25 mm. from the bottom a hole about 3 mm. wide is bored in the wall of the tube to allow condensed liquid to drop. The tube is 30 cm. long, and in the upper part is a roll of ordinary filter-paper, 100 cm. in length, to retain moisture, and, 2 cm. above this, the band of mercuric chloride paper. The latter is prepared by immersing Whatman drawing paper for about ten minutes in 5 per cent. mercuric chloride solution, drying it at the ordinary temperature, and storing it in the dark. With a band 5 mm. in width and 12 to 15 cm. long, as much as 0.1 mgrm. of arsenic may be estimated. For comparison, bands corresponding with quantities of arsenic varying from 0.0001 to 0.1 mgrm. may be prepared. Eight grms. of zinc and 60 c.c. of 1 : 5-sulphuric acid are suitable quantities, and the total volume of the solution, after treatment with permanganate and hydrogen peroxide, is made up to 75 c.c.

T. H. P.

Detection and Estimation of Platinum in Ores. C. W. Davis. (*Technical Paper* 270, U.S. Bureau of Mines, 1921, pp. 27.)—This publication is a compilation of published methods for determining platinum in low-grade and base-metal ores. Regarding claims made from time to time that platinum occurs in some ores in such a form as to escape detection by fire assay, the opinion of a number of authorities is quoted, to the effect that such claims are groundless. W. R. S.

Estimation of Small Quantities of Zinc. M. Bodansky. (*J. Ind. Eng. Chem.*, 1921, 13, 696-697.)—A turbidimetric method is described and recommended for the estimation of small quantities (less than 5 mgrms.) of zinc in foods, etc. A weighed quantity of the substance is treated with sulphuric acid and nitric acid, incinerated, the ash is extracted repeatedly with hot dilute hydrochloric acid, the solution is filtered, and evaporated to dryness; the residue obtained is dissolved in 2 c.c. of concentrated hydrochloric acid and 50 c.c. of water, any copper present is precipitated as sulphide and removed by filtration, and the filtrate is boiled to expel hydrogen sulphide. After cooling, the solution is neutralised with ammonia, 10 c.c. of 50 per cent. citric acid solution are added, and the mixture is boiled; if calcium citrate does not separate, small quantities of calcium carbonate are added until a precipitate of about 1 gm. of calcium citrate has formed. Hydrogen sulphide is then passed into the mixture, and after several hours the precipitate is collected on a filter, washed with 2 per cent. ammonium thiocyanate solution, and dissolved in hot dilute hydrochloric acid. If the solution exhibits a red coloration due to the presence of ferric thiocyanate, the zinc must be reprecipitated; a turbidity due to

colloidal sulphur may be dispelled by boiling the solution. The latter, or an aliquot portion of it, is then diluted in a Nessler cylinder to 45 c.c.; a series of standards is prepared in other cylinders, each containing a known amount of zinc and 3 c.c. of hydrochloric acid and diluted to 45 c.c. Five c.c. of 3.48 per cent. potassium ferrocyanide solution are added to each cylinder, the contents mixed, and the turbidities compared. The formation of a precipitate of calcium citrate, either from calcium already present or from the added calcium carbonate, ensures the retention by filter-paper of all the zinc sulphide; otherwise only from 30 to 60 per cent. of the sulphide suspension is retained by filter-papers of good make. W. P. S.

Cyanometric Assay of Nickel. G. H. Stanley. (*J. S. African Assoc. Anal. Chem.*, 1921, 10, 12; *Chem. Abstr.*, 1921, 15, 2048.)—When iron is precipitated with ammonia in the presence of nickel a certain amount of the latter is invariably carried down. This may be prevented by effecting the precipitation of the iron in presence of an excess of potassium cyanide, the resulting potassium nickel cyanide not being absorbed by the precipitate. *Nickel in Steel.*—Two grms. of the sample are dissolved in hydrochloric acid, and the solution oxidised with nitric acid, treated with 3 to 4 c.c. of dilute sulphuric acid and nearly neutralised with ammonia. A measured quantity of potassium cyanide solution is added, then, sufficient ammonia to precipitate the iron, and the liquid made up to 500 c.c., shaken, and filtered. A few drops of 10 per cent. potassium iodide solution are added to 50 or 100 c.c. of the filtrate, and the potassium cyanide present is titrated with standard silver nitrate solution.

Estimation of Vanadium and Chromium in Ferrovandium by Electro-metric Titration. G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright. (*J. Ind. Eng. Chem.*, 1921, 13, 939-941.)—The method depends on the oxidation of both vanadium and chromium by persulphate, and on the oxidation of vanadium, but not of chromium, by nitric acid. Three grms. of ferrovandium are dissolved in 75 c.c. of nitric acid (sp. gr. 1.13), 10 c.c. of hydrochloric acid (sp. gr. 1.20) and a few drops of hydrofluoric acid are added to obtain complete solution, and the solution is evaporated after the addition of 50 c.c. of sulphuric acid (sp. gr. 1.58); the residual acid solution is diluted, filtered, and the filtrate made up to 1,000 c.c. One hundred c.c. of this solution are then treated with 25 c.c. of sulphuric acid (sp. gr. 1.58), 175 c.c. of water are added, the mixture is boiled, and 20 c.c. of 10 per cent. ammonium persulphate solution, and 10 c.c. of 0.25 per cent. silver nitrate solution are added; if the ferrovandium does not contain manganese, a small quantity of the latter may be added, as the persistence of the permanganate coloration is an indication that sufficient persulphate has been used. The solution is then boiled for ten minutes, 5 c.c. of hydrochloric acid (1 : 3) are added, the boiling continued for a further five minutes, and the solution is treated with 25 c.c. of sulphuric acid, cooled to 5° C., and titrated with standardised ferrous ammonium sulphate solution, the end-point being determined electrometrically. This titration measures the chromium and vanadium together. Another portion of 100 c.c. of the original solution is treated with a few c.c. of ferrous sulphate solution, boiled for several minutes, 20 c.c. of sulphuric acid and 40 c.c. of nitric acid (sp. gr. 1.40) are added, together with suffi-

cient water to make the volume of the mixture up to 200 c.c., and the boiling is then continued at such a rate that the volume of the solution is reduced to 100 c.c. in one hour. The solution is next diluted, cooled to 5° C., and titrated with ferrous ammonium sulphate solution. This titration gives the amount of vanadium present and the difference between the two titrations is a measure of the chromium.

W. P. S.

Volumetric Estimation of Ammonium Salts by Means of Formaldehyde.

I. M. Kolthoff. (*Pharm. Weekblad*, 1921, **58**, 1463-1469.)—The method devised by Gaillot for the estimation of ammonia in its salts is based on the reaction with formaldehyde— $6\text{HCOH} + \text{NH}_3 \rightarrow (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$ —and titration of the acid liberated from the salt. This gives results about 5 per cent. too low. In the method of van Bers (*Chem. Weekblad*, 1917, **14**, 968), in which the ammonium salt is left for three to six hours in contact with excess of formaldehyde in an alkaline medium, and the excess of alkali titrated, the results are 0.25 to 0.5 per cent. too high. Contrary to the statement of van Bers, the titration can be accurately effected directly, with phenolphthalein as indicator, provided that a sufficient excess of formaldehyde be added and the mixture allowed to stand for a minute before the titration. In the case of pure ammonium salts, 25 c.c. of an approximately 0.1 mol. solution are treated with 5 c.c. of formaldehyde solution (which must be neutral to phenolphthalein) and 2 to 3 drops of a 1 per cent. solution of phenolphthalein, and the mixture shaken, allowed to stand for one minute, and titrated with $\frac{N}{10}$ alkali, 1 c.c. of which corresponds with 1.8 mgrm. of ammonium. The ammonium salt solution should previously be rendered neutral to methyl red, which is the only indicator that should be used with the ammonium salts of strong acids. Pure ammonium salts of weak acids, such as ammonium acetate, react with methyl red in alkaline solution. In such cases the solution should be brought to the correct P_H value. Thus, in the case of an ammonium acetate solution with $P_H = 7.0$, the amount of free acid or free base can be calculated by titrating the liquid, in presence of neutral red, to a titration exponent $P_T = 7.0$ (Kolthoff, *Pharm. Weekblad*, 1920, 57). In the reciprocal method, in which formaldehyde is estimated by treatment with ammonia, the excess of which is subsequently titrated, it is not possible to get a sharp end-point with any indicator. The best results are obtained by the use of an indicator, such as neutral red or phenolsulphophthalein, which changes colour at about $P_H = 7.0$.

Volumetric Analysis of Mixtures of Permanganate, Dichromate, and Chromic Salts. **N. G. Chatterji.** (*Chem. News*, 1921, **123**, 232-233.)—(a) *Mixture of permanganate and dichromate.* A portion of the solution is titrated with standard ferrous sulphate solution to a permanent pink end-point, thus giving the total iron equivalent. In another portion of the solution the permanganate is converted into insoluble hydrated manganese dioxide by adding a hot solution of manganese sulphate and zinc sulphate (or a soluble salt of magnesium, calcium, or strontium), the manganese dioxide is filtered off, and the dichromate in the filtrate is titrated with standard ferrous sulphate. The composition of mixtures of (b) *dichromate and chromic salts* and (c) *permanganate and chromic salts* may be determined by making

use of the fact that chromic salts are converted into dichromate by oxidation in acid solution with hydrated manganese dioxide. The manganese dioxide is prepared by adding permanganate solution drop by drop in slight excess to a solution of manganese sulphate containing sodium nitrate; the precipitated manganese dioxide is filtered off, washed with hot water until free from electrolytes, and dried at 40° to 45° C. In the case of (b) dichromate originally present is estimated by titration with ferrous sulphate; the chromic salt present in another portion of the solution is then oxidised by boiling for a few minutes with manganese dioxide and dilute sulphuric acid, and, after filtration, the total dichromate is titrated. In the case of (c) the chromic salt is oxidised to dichromate by means of manganese dioxide, and the total oxidising value of the permanganate and dichromate determined by titration with standard ferrous sulphate; then, in another portion of the solution, the permanganate is converted into manganese dioxide (by treatment with manganese and zinc sulphates, as in (a)), and the chromic salt oxidised by means of manganese dioxide to dichromate and estimated by titration with standard ferrous sulphate.

R. G. P.

Rapid Method for the Estimation of Phosphoric Acid. H. Copaux.

(*Comptes rend.*, 1921, **173**, 656-658.)—This method is based on the fact that when phosphoric acid, mixed with another acid, such as hydrochloric or sulphuric acid, is shaken with ether and an alkaline molybdate solution, the resulting phosphomolybdic acid combines with the ether and water to give a dense, yellow liquid immiscible with the mother-liquor. This liquid has the specific gravity 1.23 at 20° C. and varies slightly in percentage composition, three analyses giving the following limits: P_2O_5 , 1.66-1.84; $P_2O_5 + MoO_3$, 43.56-44.18; $(C_2H_5)_2O$, 32.27-33.46 and H_2O , 20.40-22.90; these results agree approximately with the formula, $P_2O_5 \cdot 24MoO_3 \cdot 3H_2O + 96H_2O + 37(C_2H_5)_2O$. The volume of the liquid formed by 0.001 gm. of P_2O_5 is calculated to be 0.05 c.c., but for practical purposes this is actually determined, as described below. The apparatus used consists of a glass bulb of 60 c.c. capacity, with a short neck and flanged mouth and an extension below in the form of a tube which is 80 mm. long and 6 mm. in bore, and is graduated in tenths of a c.c. The reagents employed are: (1) A solution containing 200 grms. of H_2SO_4 per litre; (2) sodium molybdate solution prepared by dissolving 100 grms. of molybdic anhydride in a hot solution of 32 grms. of sodium carbonate in water and making up to 1 litre; (3) alcohol-free ether; (4) a standard solution of about 5 grms. of ammonium dihydrogen phosphate per litre, the strength of which should be estimated gravimetrically, since the percentage of phosphoric anhydride in the commercial salt is often below the theoretical value, 61.73. The liquids should be added in a certain order and should be intimately mixed at once: 10 c.c. of the standard solution, 10 c.c. of the sulphuric acid, and sufficient ether to give a supernatant layer 3 to 4 mm. deep, are introduced in order into the flask, which is closed by the thumb and shaken, five or six portions, making 15 c.c. in all, of the sodium molybdate solution being then added and the liquid mixed after each addition. An exactly identical mixture is placed in a second, similar flask and the two are centrifuged, a special frame being used to hold the flasks. The separation of the three phases is complete

after one or two minutes, and the volume of the phosphomolybdic liquid is then read off and the number of mgrms. of P_2O_5 corresponding with 1 division on the scale calculated. When a natural phosphate is to be analysed, 1 gm. of the substance is heated on a water-bath for ten to fifteen minutes with 3 to 4 c.c. of nitric acid and a little water. After evaporation to dryness, which may be dispensed with if accuracy is to be sacrificed to speed, the residue is diluted and the liquid filtered through a small pleated filter into a 100 c.c. flask, the filtrate and washings being made up to volume; 10 c.c. of this solution are then treated as described above. For various phosphates this method gave (1) 28.90, (2) 52.43, and (3) 27.76 per cent. of P_2O_5 , the percentages obtained gravimetrically being (1) 28.91, (2) 52.52, and (3) 27.81 and 27.93. Any citrates present must be destroyed before this method is applied.

T. H. P.

New Method for the Estimation of Silica. Travers. (*Comptes rend.*, 1921, 173, 714-717.)—This method is based on conversion of the silica into alkaline silicate, precipitation as potassium silicofluoride, which is insoluble in a solution containing 15-20 grms. of potassium chloride per 100 c.c., and titration of the moist precipitate, at the boiling-point, with $\frac{N}{5}$ -potassium hydroxide solution free from carbonate, with phenolphthalein as indicator:— $K_2SiF_6 + 4KOH = 6KF + SiO_2 + 2H_2O$ (cf. Hilemann, *Zeitsch. anorg. Chem.*, 1906, 51, 159). The alkaline solution of the alkali silicate is treated in a silver dish with at least 1 gm. of potassium fluoride per 0.15 gm. of silica present, an excess of 2 c.c. of ordinary hydrochloric acid over the amount required to produce neutrality towards methyl orange being then added, and afterwards at least 7-10 grms. of solid potassium chloride per 50 c.c. of liquid. The potassium silicofluoride is collected on a hardened filter-paper supported on an ebonite or papier-mâché funnel and is washed with either 20 per cent. potassium chloride solution or 50 per cent. aqueous alcohol until the washings fail to react acid towards methyl orange, and afterwards titrated with standard potassium hydroxide solution: 1 c.c. of $\frac{N}{5}$ -potassium hydroxide corresponds with 0.005 gm. of silica. The proportions of silica present in the potassium chloride employed and in the potassium hydroxide used to convert the silica into alkali silicate are determined by a blank estimation and applied as a correction. With quartz or a silicate the silica is converted into alkali silicate by fusion with potassium hydroxide in a silver crucible, the mass being taken up in water and filtered boiling into a silver dish; the cold solution is then treated as described above. When alumina is present, insoluble alkali silico-aluminate is formed and remains on the filter; in this case the moist precipitate is placed in the filtrate, nitric acid is used for the neutralisation instead of hydrochloric acid, and potassium nitrate is taken in place of the chloride, so as to avoid formation of silver chloride owing to the crucible being slightly attacked. The method serves for the estimation of silica in presence of fluorine, and if the proportion of fluoride present be sufficient, potassium fluoride need not be added.

T. H. P.

Estimation of Thiocyanates in the Presence of Salts Precipitated by Silver Nitrate. A. Dubosc. (*Ann. Chim. anal.*, 1921, 3, 297-298.)—In

cases where salts yielding precipitates with silver nitrate are present (*e.g.*, in ferrocyanide mother-liquors), it is impossible to titrate the thiocyanate with silver nitrate. The author, therefore, oxidises the sulphur present in the thiocyanate to sulphuric acid, and estimates this as barium sulphate. As an oxidising agent a neutral solution containing 2 grms. of active chlorine per 100 c.c. is prepared by electrolysing sodium or magnesium chloride, a suitably cooled anode being used. For the estimation a quantity of the sample (equivalent to 0.2 to 0.4 gm. of barium sulphate) is dissolved in 50 c.c. of water, 50 c.c. of barium chloride solution (4 per cent.) are added, and then 50 c.c. of the oxidising agent, with constant agitation; after standing for ten minutes the liquid is acidified with hydrochloric acid, and the barium sulphate precipitated, washed, etc., in the usual manner. Any soluble sulphides present are converted into insoluble sulphides and removed before the estimation of thiocyanate, whilst any sulphates are estimated separately and an allowance made. The method has given concordant results in the analysis of residual liquors from the manufacture of ferrocyanides.

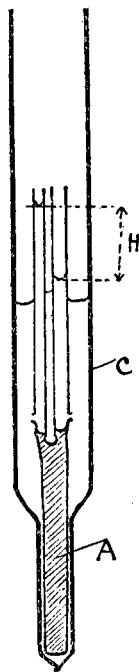
R. G. P.

PHYSICAL METHODS, APPARATUS, ETC.

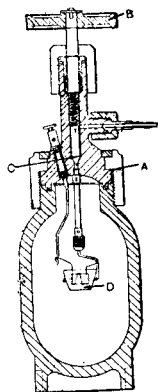
Determination of Surface Tension from the Rise in Capillary Tubes. S. Sugden. (*J. Chem. Soc.*, 1921, 119, 1483-1492.)—Considerable errors have been introduced in many determinations of surface tension by the capillary-tube method owing to the wide tube used not being large enough to give a plane surface from which to measure the rise. The use of very wide tubes is inconvenient and requires large quantities of liquid. The method proposed by the author depends upon the difference of level in two capillary tubes, and eliminates this source of error. The apparatus illustrated is easily made and admits of very accurate results. Two narrow pieces of quill tubing of different diameters (tested by the microscope and by a column of mercury for uniformity of bore), 5 cms. in length, are fused together on to a piece of glass rod A, and a small hole is blown in the base of each. The whole is supported in the wide tube C as illustrated. The difference in level (H) is measured with the travelling microscope, and the surface tension (γ) is calculated from the equation,

$$2\gamma \left(\frac{1}{b_1} - \frac{1}{b_2} \right) = Hg (D - d),$$

where b_1 and b_2 are the radii of curvature of the meniscus in the tubes of radius r_1 and r_2 ; D is the density of the liquid, and d that of the level of the air and/or vapour; g is the acceleration due to gravity. Tables are given for calculating b_1 and b_2 when r_1 and r_2 are known. The theory of the capillary-tube method is also discussed.



H. E. C.



Determination of the Calorific Value of Coal. F. S. Sinnatt and M. B. Craven. (*Lancs. and Cheshire Coal Research Assoc.*, 1921, Bulletin 10, pp. 23.)—

The calorimetric methods officially used by the Association are: (a) by means of the sodium peroxide calorimeter, and (b) the bomb calorimeter. With the former apparatus a mixture of granular coal and sodium peroxide is burned in a closed nickel crucible immersed in water (*cf. Parr, J. Ind. Eng. Chem.*, 1919, 2, 235), whilst with the bomb calorimeter, the Mahler-Kroecker and the Mahler-Cook forms of which are described, the coal is burned in compressed oxygen. The Mahler-Cook calorimeter has several advantages over the other form; it consists of a steel bomb immersed in a copper vessel containing water, and has a stirrer actuated by a small electric motor. The bomb has a water-equivalent of about 650 grms. as compared with 370 grms. for the Mahler-Kroecker bomb. Its head consists of a powerful hexagon nut, fitted by means of a special spigot joint, A, so that the crucible and its contents are not disturbed during manipulation, as is the case with the Mahler-Kroecker form. Since the lead washer is not rotated when fixing the head, the wear on this part experienced in the Mahler-Kroecker apparatus is avoided. Inlet and outlet tubes, with cone valves C, are fitted to the head, and the platinum or silica crucible D, suspended in the centre of the bomb, is provided with a platinum wire connected with a source of current for ignition of the coal. The valve for the introduction of oxygen is controlled by a hand-wheel, B, 3 inches in diameter. The whole apparatus is enclosed in a chamber with a sliding glass door, outside of which are a cathetometer for reading the thermometer, the motor for actuating the stirrer, and the switches and resistance for regulating the igniting current. For accurately determining the water-equivalent of the apparatus a substance of known calorific value, preferably benzoic acid, is employed. After the completion of a combustion the gases are allowed to escape, and the bomb and head washed out with distilled water, the liquid being titrated with $\frac{N}{10}$ sodium hydroxide solution, with methyl orange as indicator. It is then slightly acidified with hydrochloric acid, filtered, and treated with barium chloride solution, and the percentage of sulphuric acid calculated. By deducting the volume of $\frac{N}{10}$ sodium hydroxide solution to which this is equivalent from the volume used in the titration, the percentage of nitric acid formed by the combustion may be deduced. If the percentage of sulphur present in the coal is known, the amount of sulphuric acid formed may be accurately calculated, the barium chloride precipitation being thus avoided. The amount of sulphur remaining in the ash is small, and, if the ash does not exceed 10 per cent., the error introduced by this rapid modification is not important. Details are given of the various corrections to be applied in accurate determinations.

T. J. W.



REVIEWS.

THE PHYSICAL PROPERTIES OF COLLOIDAL SOLUTIONS. By E. F. BURTON. Second Edition. Pp. viii + 221. London: Longmans, Green and Co. Price 12s. 6d.

The new edition of Burton's work forms a welcome addition to the rapidly growing literature of colloids. The comparative novelty of the subject, and its bearing on many and diverse branches of science, has led to its being treated by authors with widely different training and predilections, and it is of interest to see the treatment accorded to it by the physicist. It is, no doubt, natural that the latter should prefer one main class, the suspensoid colloids—with which the book concerns itself almost exclusively—since they have been the subject of brilliant theoretical investigations.

These receive full justice in the present work. A long and admirable chapter is devoted to the Brownian movement, in which the work of v. Smoluchowski, Einstein, Langevin, and Perrin is summarised lucidly. The author makes an original contribution by demonstrating why the law of logarithmic distribution cannot hold for any but small heights—a point, occasionally raised by intelligent students, and on which the existing textbooks preserve reticence. The theory of the ultra-microscope, and of the optical properties of systems of small particles, is also given very fully. In this connection the extremely curious case of the blue sulphur suspensions (*i.e.*, blue in *transmitted* light) described by Porter and Keen (1913), and quite recently (1920) by Auerbach, might have been mentioned, as presenting a problem of extraordinary difficulty, which awaits attack.

The treatment of the electrical properties, a portion of the subject which owes a good deal to the author, and of the cognate phenomenon of electrolyte coagulation, is equally full and clear, and the author gives due weight to recent criticisms of the "valency rules." He still, however, considers surface tension an operative factor in coagulation or coalescence, a position criticised—effectively, as it seems to the reviewer—by Zsigmondy, and ignored by v. Smoluchowski.

The investigations of Debye and Scherrer (begun in 1917) on the structure of ultra-microscopic particles as revealed by X-ray interference should also have been mentioned, as the proof that such particles have the same space lattice as, say, solid gold or silver, is of the greatest interest.

This, and a few minor omissions, in no way detract from the value of the book, which is to be thoroughly recommended to every serious student who is not deterred by formulæ containing even complex quantities. The style and printing conform to the high standard of the series, and the proof-reading has been quite exceptionally careful.

EMIL HATSCHKE.

FACTORY CHEMISTRY. By W. H. HAWKES, M.Sc. Pp. 59. London: Longmans, Green and Co. Price 4s. 6d. net.

The reviewer is often tempted to quote, "A little knowledge is a dangerous thing," but is generally restrained from doing so by the fear of being thought commonplace, or perhaps by the feeling that all knowledge is useful and that any

attempt to popularise chemistry is in some degree commendable. Unfortunately, perusal of the present little book, "especially designed for factory men interested in the study of chemistry as it bears on the various operations in factory practice," seems likely to prove more dangerous than helpful. In the short space of 59 pages (small pages of comparatively large type at that) it is rash to attempt even a rough outline of the essential framework of chemistry, and when one considers that this is attempted in the first 36 pages, leaving the remainder for qualitative analysis, it is obvious that the attempt is foredoomed to failure. There are already available many excellent elementary books on chemistry; the present seems superfluous and more likely to prove harmful than otherwise.

R. G. PELLY.

THE ELECTRIC FURNACE. By J. N. PRING. Pp. 485. (Monograph in the series by Sir E. THORPE, C.B., F.R.S.) London: Longmans Green and Co. Price 32s. net.

The progress in electric furnace design and operation both for electro-thermal and electrolytic purposes has, during the last few years, been extremely great—a fact which is well exemplified by reading this volume after a glance at Dr. Pring's previous publication in this field. In 1908 his previous work, a small volume to the Gartside Scholarship electors, appeared, entitled "Some Electro-chemical Centres," in which typical applications of the electrical methods were discussed. In the present volume the reading matter, which is illustrated with excellent drawings and photographs, is equally divided between the design and operation of various types of furnaces and their application to high temperature chemistry.

To the analytical and research chemist the chapter on experimental furnaces, and more especially the brief description in another part of the volume of the Northrup Induction Furnace, will prove of interest. In this ingenious furnace any object may conveniently be heated in its container—*e.g.*, a piece of metal in a glass globe without the insertion of any leads or electric contacts. The chapters on the exact measurement of temperature, on furnace refractories, and on the heat losses through walls and electrodes, form one of the most valuable features of the book, since they deal with points frequently neglected, even by careful investigators, and on which reliable data are not readily attainable.

The chapters on power supply, both water and steam, contain pre-war working cost and post-war estimates derived from various sources. The possibility of enlarging the English electro-chemical industry by further utilisation, on the one hand of river power or tidal energy, as in the contemplated Severn barrier, and, on the other, from coal, is fully discussed. Calculations based on what is generally termed the low temperature carbonisation process have always to be received with caution. From the national and scientific point of view the process is fundamentally desirable, but economically must still be considered distinctly hazardous. Owing to the small hourly output per cubic foot of retort space in the plant, and the possibility of extreme fluctuation in by-product prices, most of the attractiveness of the proposal is lost, unless smoke-abatement legislation, either municipal or national, assures a market for the solid fuel produced.

The chapters on carbide manufacture and nitrogen fixation are short, compre-

hensive, and clear, although the section on the Haber process is, unfortunately, somewhat limited. In discussing the effect of poisons on the platinum catalyst employed in the catalytic oxidation of ammonia, phosphorus is included. The more recent investigations in this field have shown that in this reaction, presumably on account of the somewhat elevated temperature, no anti-catalytic effect can be observed.

Over 120 pages are devoted to electro-ferro-metallurgy, and it is in this field that electrical methods have made the most striking advances during the last decade. Both the thermal and hydro-metallurgy of zinc are described; in the former section the blue powder problem is given scarcely adequate treatment, although a problem more cogent to the subject-matter of the volume than the second section. This is altogether a very readable book.

ERIC K. RIDEAL.

PERFUMES, ESSENTIAL OILS, AND FRUIT ESSENCES USED FOR SOAP AND OTHER TOILET ARTICLES. By GEOFFREY MARTIN, D.Sc., F.I.C. Pp. viii + 138. London: Crosby, Lockwood, and Son. 1921. Price 12s. 6d. net.

In the preface to this work we are told that there exists a need for a short and clear account of the principal scenting substances used in practice, especially in the soap industry, together with practical directions for testing them, so that the works chemist or the manufacturer can speedily find the article he desires, and also test its qualities by a determination of its contents. "This small book is written to supply this requirement."

The work is divided into thirteen short chapters, the first commencing with a reference to the literature of the subject. It is an unfortunate start, as the "Chemistry of Essential Oils" is referred to in its second edition, 1908, whereas there is a third edition dated 1918, and a fourth edition dated 1921. Gildemeister and Hoffmann's second edition is only quoted as the 1910 edition, whereas there were two volumes published in 1913. In this chapter five pages are devoted to a table containing Erdmann's classification of perfumes, which is obsolete, useless, and fragmentary.

The manufacture of essential oils and perfumes is dismissed in two pages of letterpress. In a few lines a method of expression of essential oils is described, and this is followed by the statement that "the rinds of such fruits as limes, lemons, oranges, bergamots, are rich in essential oils—the so-called citrus oils—and much attention has been directed in recent years to expressing these oils economically from them, an object all the more important, as these rinds are, to a great extent, a waste product."

Not a hint of the method by which lemon and orange oil are, in fact, prepared, is to be found, and to speak of these fruits as waste products hardly shows much acquaintance with the industry.

Chapter III., about 17 pages, is devoted to the description of "Essential Oils and other Vegetable Perfumery Substances." This chapter contains a series of short monographs on a selected number of essential oils, etc. The constants quoted are, in the main, accurate, but the remarks made do not indicate a very close acquaintance with many of the articles described.

Under Benzaldehyde, the only test suggested for chlorine is the practically obsolete one of burning filter-paper impregnated with the oil, under an inverted beaker. This test, of course, will not disclose chlorine in the quantities which commercial samples have for some years past contained.

We are told that "artificial hyacinth consists of secret blends of various ingredients. Styrolene and styrolene derivatives possess odours resembling that of natural hyacinth, and probably form the basis of these preparations admixed with terpineol and other artificial ingredients." This would scarcely help the practical man, since phenyl-acetic aldehyde is one of the most important of the artificial perfumes known.

We find that "lemon oil is often adulterated with turpentine and with oil of orange."

Lemongrass oil is said to be frequently adulterated with turpentine. The reviewer has examined many hundreds of market samples, but has never found or heard of this adulterant.

Artificial neroli oil certainly should contain a little indol, but 30 per cent. is, with this evil-smelling body, surely out of the question.

The main constituents of patchouli oil are given as patchuliol (97 per cent.) and cadinene. It is difficult to know where this statement can be traced to. In 1904 Schimmel and Co. published an investigation in which they stated that about 97 per cent. of the oil consisted of bodies that have no odour value, and that they had identified quite a number of bodies, which need not be reproduced here. Artificial Rore oils, "being mixtures of citronellol, geraniol, linalol, phenyl-ethyl alcohol, and citral," would, we think, scarcely suit a discriminating perfumer to-day. West Australian sandalwood oil is stated to contain santalol as its main constituent, with esters of santalol, and santalal. Of this no evidence is available, and it is almost certainly inaccurate.

In the short chapter on artificial and synthetic perfumery substances a clear and accurate distinction between artificial and synthetic perfumes is drawn. In spite of this distinction, the author classes as "synthetic (simple) perfumes, many of which occur naturally in essential oils" such bodies as geraniol, linalol, menthol, santalol, etc.

Although ionone of commerce is and has been sold as 100 per cent. for many years, it is stated that it is usually sold in a 10 per cent. alcoholic solution. This *was* true in the bygone days before the patent expired, but is not so now.

In this chapter, and in the chapter dealing with artificial fruit essences, no reference whatever is made to a large number of synthetics which have, during the past seven or eight years, appeared on the market, and which are used by nearly every experienced perfumer, and without which the distinctive character of his products would be lost.

A good deal of space is devoted to formulæ for perfumes, which are of the usual character, and are usefully collated for the practical perfumer—so long as he does not aim at being right up to date. Four pages are devoted to the analysis of essential oils and perfumes. Obviously this is dealt with in mere outline, but we cannot conceive anyone determining the m.-pt. of an essential oil in the following

manner: "Some of the solid oil or crystals is melted and sucked up a glass capillary tube, which is attached to the bulb of a thermometer immersed in a bath of water, glycerine, or oil. The temperature of the bath is increased until the crystals in the tube melt and rise to the surface. This is regarded as the m.-pt." This book is very disappointing, and it is difficult to see what class of works chemist or manufacturer it will seriously assist if he really wishes thoroughly up-to-date knowledge, and anything more than a rudimentary acquaintance with the examination of his raw materials.

ERNEST J. PARRY.

FORENSIC CHEMISTRY. By A. LUCAS, O.B.E., F.I.C. Pp. vii + 268. London: Arnold and Co. Price 15s. net.

When the author's small book on legal chemistry was reviewed in the *ANALYST* (1920, 45, 245) it was suggested that as there was no English text-book on the subject, that collection of notes might well be made the nucleus of a general treatise on forensic chemistry. The present work is the outcome of that suggestion, and the wealth of new material which has now been made available will be welcomed by both the chemical and medical professions.

As Director of the Government Laboratories at Cairo, Mr. Lucas has had exceptional opportunities for applying scientific methods to the investigation of every description of crime, and, although such work does not come as a matter of routine to many chemists, there are few who do not, at some time or other, have to solve problems coming within the scope of the subject matter of this work.

The book is divided into a short introduction and twenty-one chapters, conveniently arranged in the alphabetical order of their contents, and has a good index, and at the end of each chapter up-to-date references are given to the cognate scientific literature.

The introduction contains a concise outline of the precautions to be taken in handling and examining "exhibits" to be produced in court, and of the way in which the evidence should be presented. Incidentally it is pointed out that no attempt should be made to demonstrate an object under the microscope to a judge or jury, since it will only cause confusion in the minds of those not trained in the use of scientific instruments; and in this connection it is recalled that in the Maybrick case the judge, after trying in vain to examine an arsenic deposit with a lens, remarked of that instrument that it was very difficult to handle.

The reviewer's experience is quite in accordance with this caution. Where demonstration of minute objects is required it should be given by means of enlarged photomicrographs.

The chapters of the text deal, *inter alia*, with the investigation of blood-stains, bullets, clothing, dust and dirt, documents, fibres, finger prints, poisons, preservation of the body after death (including some interesting original observations on mummies), robbery from letters, and tobacco. Some of these subjects are also of a medical character, and in such cases the author has restricted himself to the chemical and general aspects.

The chapter on blood-stains, which includes the latest work and conclusions

on the precipitin test, has been revised by Mr. W. M. Colles, who is in charge of all such investigations for the Egyptian Government.

The chapter dealing with documents gives a comprehensive survey of the whole ground, and is illustrated by notes of various cases in which scientific methods have been applied. Many of the investigations described here are original, and the results will be of great use to other workers in this field.

Like other chemists who have specialised in the examination of documents, Mr. Lucas has been forced to take into consideration the question of handwriting. He rightly lays stress upon the importance of the observations and deductions being made only by those who are accustomed to apply scientific methods. Much of the adverse criticism upon handwriting experts has been due to the expression of dogmatic opinions by men who have had no scientific training. Thus, a leading expert of the last generation claimed infallibility for both himself and his son, and was then obliged in cross-examination to admit that, on one occasion, the two infallibles had appeared on opposite sides.

It is to guard against dangers such as this that Mr. Lucas calls attention to the precautions which should be taken before expressing any opinion on handwriting. This section also contains many interesting particulars on the special difficulties attending the examination of Egyptian writing.

It would occupy too much space to refer in detail to each of the chapters, for the author has much that is new to record in all of them, but their general character will be understood from what has been said.

It should be added that the book is clearly printed and on good paper, and the author and the publishers may be congratulated on having made such a valuable addition to the standard works on chemistry.

EDITOR.