

# THE ANALYST.

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

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ORDINARY MEETING, APRIL, 2, 1919.

HELD at the Chemical Society's Rooms, Burlington House. Dr. Samuel Rideal, President, in the chair.

Certificates were read for the first time in favour of Messrs. Charles Frederick Lee Barber, A.I.C., George Stanley Withers Marlow, B.Sc., F.I.C., and Frederick William Read.

Certificates were read for the second time in favour of Messrs. Madanlal Jekisandas Gajjar, and James Sorley, F.I.C.

The following were elected members of the Society: Messrs. Robert Odell Bishop, A.I.C., Hubert William Bywaters, D.Sc., Ph.D., F.I.C., Bernard Scott Evans, M.C., B.Sc. (Lond.), F.I.C., Frank Scott Fowweather, M.Sc., A.I.C., Robert Atkinson Oddy, William Branch Pollard, and Charles Kenneth Tinkler, D.Sc., F.I.C.

The following papers were read: "A Method for the Determination of Monochlorbenzene in Mixtures Containing Benzene, Monochlorbenzene, and Dichlorbenzene," by N. G. S. Coppin, M.Sc., A.I.C., and F. Holt, O.B.E., M.Sc., A.I.C.; "The Electrical Conductivity of Milk," by J. H. Coste, F.I.C., and E. T. Shelbourn, F.I.C.; and "Note on Soluble Lead in the Glaze of Casseroles," by Helen Masters, B.Sc.

The President reported to the meeting that, as a delegate appointed by the Council, he had attended a meeting of the Committee on the Standardisation of Laboratory Glassware, when an interim report of that Committee was being drafted, and he had been asked to ascertain the views of the Society on the sizes of beakers in common use, with a view to their manufacture in standard series.

He announced that the Committee had recommended that beakers should be catalogued in future as to their height, their diameter in millimetres measured immediately above the bottom curve, and the approximate total capacity in cubic centimetres to running-over point, and that this should apply also to beaker-flasks and conical beakers.

It was further decided that beakers should be manufactured in two series—squat and tall—the squat forms to be with or without spouts. In order to facilitate manufacture, the Committee thought that the range of diameters and tapers should

be the same for both series. The Committee wish to reduce the number of sizes manufactured to a minimum consistent with the requirements of users, and it is important that the beakers should nest and pack properly.

The point which the Committee had asked him to ascertain from practising analysts was which of the two nests of tall forms shown in the blue prints would be most acceptable to analysts, and after members had had an opportunity of studying the prints, he would be glad of an expression of opinion which he might report to the Committee.

Following a discussion it was decided to ask the President to point out that the quality of the glass was one of the most important factors in arriving at a useful beaker ; that smaller sizes than the tall forms in either blue print were in common use ; that those with 10 and 20 c.c. capacity should be included in the series ; that it was seldom that the very large beaker of 4 to 5 litres was required, so that if the series was to be limited in number members would prefer the capacities to range from 10 and 20 to 4,000 c.c. ; that the very tall forms did not seem to be necessary, and were, indeed, undesirable for various reasons, the shorter of the two " tall " forms being far preferable ; and that it was important in the case of the spouted squat form to ensure that the lip be recurved so as to prevent dripping.

The President promised to report these views to the Sub-Committee in due course.



### THE ELECTRICAL CONDUCTIVITY OF MILK.

By J. H. COSTE, F.I.C., AND E. T. SHELBOURN, F.I.C.

*(Read at the Meeting, April 2, 1919.)*

THE proportion of ash yielded on the incineration of milk is recognised as being fairly constant at rather over than under 0.7 per cent. It therefore appeared probable that the electrical conductivity of milk should yield a fairly exact indication of the amount of dilution with water. Our experiments show that this is the case when a known milk is diluted (*cf.* Fig. 2.), but the examination of upwards of 200 samples of milk which, on the Board of Agriculture standard of 8.5 per cent. of solids-not-fat, appeared to be unwatered, has convinced us that, although the majority of samples fell within fairly close limits of specific conductivity— $K_{15} = 0.0040 - 0.0042$ —the value is not sufficiently well defined to make the determination generally useful for detecting adulteration. It would, however, be useful in a large dairy or institution as a check on watering of milk which had already been examined by the conductivity method, and which had afterwards passed through various hands. Before arriving at these conclusions we investigated the effect of certain factors on the electrical conductivity. We find that—

1. The temperature co-efficient of electrical conductivity in the region of 15° C. is 0.000093, or about 2.3 per cent. of the total conductivity. This agrees fairly with the normal value of 0.026 K for neutral salts.

The electrical conductivity of presumed genuine milks may vary from  $K_{15} = 0.0035$  to  $0.0047$ , but in more than 50 per cent. of the samples it was between  $0.0040$  and  $0.0042$ .

3. The electrical conductivity of milks increases, up to a certain point, with the development of acidity, but, owing to the lessened dissociation of the acids formed as their concentration increases, it reaches an almost constant value, whilst the amount of acid is still increasing.

4. There is no correlation between electrical conductivity and total solids.

5. There is no well-defined correlation between electrical conductivity and total "ash."

6. There is a marked correlation between electrical conductivity and chlorine (Cl) content of milk.

7. The specific conductivity of a mixture of milk and water decreases with dilution, but the specific conductivity of the milk in the solution increases greatly as the dilution becomes greater, owing, it may be presumed, to dissociation of phosphates and citrates.

Some of these conclusions seemed to us rather difficult of explanation, but we have found that an investigation on "Milk: its Sugar, Conductivity, and Depression of Freezing Point," by Liliac C. Jackson and A. C. H. Rothera (*Biochem. J.*, 1914, 8, 1), in which they examined the milk of a great variety of mammals, throws the desired light on the question.

Jackson and Rothera point out that many workers have determined the depression of the freezing point of milk below that of water, and have concurred in the value  $\Delta = 0.56^\circ - 0.57^\circ$ . They also quote Dreser and Winter, who showed that this value was nearly the same as that found for blood,  $\Delta = 0.58^\circ - 0.59^\circ$ . This figure is a measure of the osmotic pressure, and is, of course, well known as a convenient, although not very sensitive, means of determining it. The osmotic pressure of milk is due to the milk-sugar and salts which it contains. The fat has no effect, and that of the proteins, if any, is too small for detection by a cryoscopic method. As the osmotic pressure of milk is almost constant, it follows that any variation in the proportion of lactose will be accompanied by such a variation in the salts as will maintain the proper osmotic pressure. That is, an increase in the amount of lactose will lead to a decrease, not necessarily in the amount of salts, but in the total number of their molecules and ions which will be found dissolved in the milk. The osmotic pressure of average milk appears to be made up as follows:

TABLE I.

Constituent.	Percentage.	Osmotic Pressure.	$\Delta$ .
Lactose	4.7	3.03	$0.25^\circ$
Alkali } Cl ions	0.1	1.33	$0.11^\circ$
Chlorides } (Na or K ions)			
Other salts and ions	—	2.42	$0.20^\circ$
Total	—	6.78 atmos.	$0.56^\circ$

It will be seen that alkali chlorides, from their relatively low molecular weights and highly dissociated state in only fairly dilute solutions, contribute very largely to the total osmotic pressure. For the same reason they also contribute very largely to the electrical conductivity—from, say, 50 to 80 per cent. of the whole value of  $K$  being due to chlorides (reckoned as sodium chloride). As the electrical conductivity of a solution is due to the dissociated solutes—that is, the free ions—it is evident that any variation of the lactose content of milk, accompanied, as it will be, by a compensating variation of the salt content, will cause a variation of the opposite sign in the specific conductivity. So that, although watered milks will show low conductivities, so also will very rich ones. A high conductivity with high lactose content will indicate some abnormality, either pathological or caused by addition of salts. Proteins also have a marked effect on conductivity. Every 1 per cent. protein lowers it 2.76 per cent. According to Jackson and Rothera it is not difficult to increase the conductivity by artificially causing functional disturbances of the

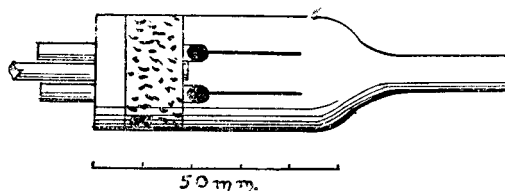


FIG. 1.

mammary gland, but it is unusual for such disturbance to alter  $\Delta$ . Hence the lactose content is low in such pathological fluids. A low conductivity with low lactose content indicates a hydropathic condition set up in the milk after leaving the udder; it is only compatible with dilution.

EXPERIMENTAL.—Most of our determinations of conductivity were made with a metre bridge with a platinum wire of about 12 ohms resistance (0.1 mm. diameter), using 100 ohms comparison resistance and obtaining the current from the secondary of a small medical coil. The telephone was of the “watch” form, having a resistance of about 40 ohms. Later we used a Kohlrausch universal bridge with a high-frequency coil and 100 ohm resistance. The wire was of platinum iridium. The method of making the determination is described in most books on practical physical chemistry. The electrodes were of the pattern shown in Fig. 1. The cork was paraffined, and the space above it filled in with sealing-wax to make the arrangement rigid. The platinised platinum electrodes were 19 mm.  $\times$  3 mm., and 4 mm. apart. The constant of the system—about 0.35—allowed the reading to come fairly near middle of the bridge wire. The determination was made at the temperature of the milk and corrected to 15°.

1. *The Temperature Coefficient*, as already stated, was found to be approximately 0.000093 or  $0.024K_{15}$ , the value which might be expected of a dilute saline solution.

2. *The Electrical Conductivity of presumed Genuine Milks*.—Two hundred and three in all were examined, of which nine were from individual Jersey and Short-horn cows belonging to our colleague, Dr. F. N. K. Menzies, who kindly supervised

the collection of these samples, and the remainder were obtained commercially from retailers in various districts of London. The following table shows the percentage numerical incidence of the values found within each ten units in the fifth place of decimals, the observed third and fourth places being shown (*e.g.*, 40 includes  $K = 0.00400-409$ ).

TABLE II.

$K_{15} \times 10^4$	...	...	...	35	36	37	38	39	40	41	42	43	44	45	46	47
Percentage number of samples	...	...	...	1.5	0.5	3.4	4.4	10.8	26.6	26.1	16.3	5.9	3.4	0	0	1.0
Solids-not-fat ...	...	...	...	9.3-10	9.9	8.5-9.7	8.5-9.7	8.5-9.5	8.5-9.8	8.5-9.5	8.5-9.7	8.6-9.6	8.5-9.0	—	—	8.7-8.8

3. *The Influence of Free Acid* was first noted in a milk which on examination gave  $K_{15} = 0.00521$ . The acidity was found to be  $56.2^\circ = 0.056$  N. This was kept for a week, during which the acidity went up to  $87^\circ = 0.087$  N, reaching this point in six days. The conductivity was stationary at 0.00572 in two days. Formalin had been added to this sample. Another untreated "nursery" milk had an acidity of  $20^\circ$  about twenty-four hours after delivery, which went up to  $80^\circ$  in four days, and in eleven days reached  $93^\circ$ . The conductivity, originally 0.00411, went up to 0.00530 in four days, and did not materially increase in eleven days.

The grouping around the position of greatest density—*i.e.*, between  $K \times 10^4 = 400$  and  $= 420$ —is normal.

4. *The Relation between Non-Fatty-Solids and Conductivity* follows no law. The range of solids-not-fat for the above conductivities is shown in Table II. One hundred and twenty-four samples containing solids-not-fat 8.5 to 8.9 inclusive had conductivities from 0.0037 to 0.0047, and seventy-nine containing solids-not-fat 9.0 to 10.0 had an exactly similar range, the position of greatest density in each series being approximately the same—0.0040-42.

The nine samples from individual cows contained from 9.3 to 10.0 per cent. solids-not-fat. Average 9.6. The conductivity varied from  $K_{15} = 0.00350$  to 0.00388—all very low, illustrating Jackson and Rothera's generalisation.

5. *Relation between "Ash" and Conductivity.*—The percentage of ash in 195 samples varied from 0.62 to 0.85, the mean being 0.72. This was also the position of greatest density.

TABLE III.

Percentage of ash (below) ...	...	...	...	0.66	0.66-7	0.68-9	0.70-1	0.72-3	0.74-5	0.76-7	0.78-9	0.80-1	0.82-3	0.84-5
Percentage number of samples	...	...	...	1	4.1	11.8	23.1	25.2	15.4	13.3	3.6	1.5	0.5	0.5
$K_{15} \times 10^4$	...	...	...	39	37.42	37.44	37.44	37.43	35.47	35.42	42	40.44	35.33	38

The ash in the milks of individual cows varied from 0.73 to 0.85 per cent., the average being 0.79, and the median 0.80 per cent.

In each of the more frequent ranges of ash the greatest density was around  $K = 0.0040$ . "Ash" is, of course, a rather unmeaning figure in such a case as milk, and has not any necessary exact relation to the salts actually dissolved in the milk.

6. *Relation between Cl Ions and Conductivity.*—The concentration of Cl ions in milk is about 0.03 N = 0.1 per cent. Cl'. Between this concentration and infinite dilution the molecular (or specific) conductivity of alkali chlorides increases only about 11 per cent., so that the specific conductivity of their solutions will be fairly

proportional to the concentration. We have determined the chlorine in sixty-nine milks by the following process: 1 c.c. of milk is added to 0.028 gm. of pure lime (obtained by evaporating and igniting to decomposition 0.5 c.c. of a solution formed by dissolving 100 grms. of calcium carbonate in nitric acid and diluting to a litre). It is then rapidly evaporated and gently ignited. The cooled ash is then extracted with water, a drop of phenolphthalein solution added, and then sufficient sodium-bicarbonate to render the solution colourless; a suitable volume of potassium chromate solution (to make the liquid contain at least 0.1 per cent. potassium chromate), is added and the chlorine determined by Mohr's method. A small correction dependent on the volume (*v.*) of liquid at the end of the titration should be made. Hazen's value 0.003 *v.* + 0.02 c.c. is applicable if 1 c.c. silver nitrate = 0.0005 gm. Cl. It is subtracted from the volume of silver nitrate solution used, which is about 2 c.c. This method gives appreciably higher results (0.00 to 0.002 per cent. on a total of about 0.1 per cent.) than titration of the carefully determined ash. It is very rapid. We had hoped that a mixture of milk and calcium nitrate could be ignited, but found that chlorine was lost.

The chlorine in sixty-nine presumably unwatered milks varied from 0.068 per cent. to 0.143 per cent.—*i.e.*, from 0.019 N to 0.04 N. On calculating the specific conductivity for solutions of sodium chloride of the same strength, we found that more than half of the conductivity of milk was attributable to chlorides. There was a strong correlation between the proportion of Cl ions and the conductivity of the milks (see Table IV.).

TABLE IV.

Number of Milks.	Percentage of Cl.	Specific Conducting $K_{15}$ .		Mean Conductivity due to NaCl.	Mean Percentage of Conductivity due to NaCl.
		Range.	Mean.		
1.	0.06-0.69	0.00350	0.00350	0.00172	49
2.	0.07	0.0035-38	0.00372	0.00193	52
17.	0.08	0.0035-41	0.00388	0.00220	57
27.	0.09	0.0037-41	0.00399	0.00245	61
18.	0.10	0.0039-43	0.00410	0.00271	66
3.	0.11	0.0038-42	0.00403	0.00296	73
0.	0.12	—	—	—	—
0.	0.13	—	—	—	—
1.	0.14	0.00477	0.00477	0.00375	78

The chlorine in the samples from individual cows varied from 0.068 to 0.113, the average being 0.086 and the median 0.088.

7. *The Effect of Dilution.*—When milk is diluted with water the specific conductivity decreases, but at a less rate than would be attributable to mere dilution without dissociation. A series of dilutions of a milk ( $K_{15} = 0.00409$ ) with London tap-water

of such strength that each contained 0.9 of the milk in the preceding one was examined (Table V. and Fig. 2).

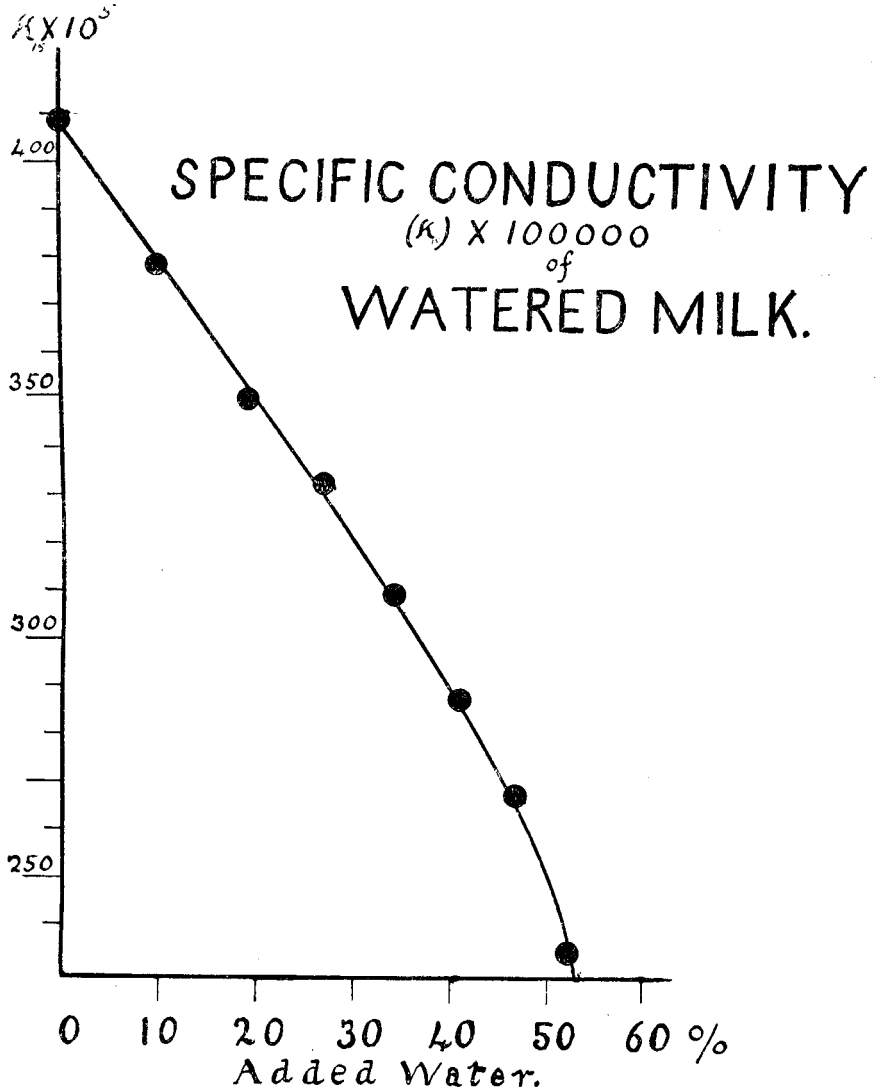


FIG. 2.

A further series, diluted with distilled water, to contain  $\frac{1}{2}, \frac{1}{4}, \frac{1}{8} \dots \frac{1}{128}$  milk, was also examined. In the latter series the specific conductivity of the milk itself more than doubled, owing to dissociation of phosphates and citrates.

TABLE V.

Milk per cent.	...	100	90	81	72.9	65.6	59.0	53.1	47.8
$10^5 K_{15}$	...	409	379	351	333	310	288	268	235

TABLE VI.

Milk	...	...	...	$\frac{1}{1}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
$10^5 K_{15}$	...	...	...	406	244	137	74	42	23	13	8
$10^5 K_{15}$ of milk in liquid	...	...	...	406	488	548	584	661	704	781	909

The conductivity falls off linearly to about 40 per cent., but in each series 50 per cent. dilution would correspond to about 60 per cent. of the original conductivity. The determination of conductivity would be useful to a milk distributor in checking the operations of a staff, but not, by itself, to the analyst dealing with milk of unknown origin.



### NOTE ON SOLUBLE LEAD IN THE GLAZE OF CASSEROLES.

BY HELEN MASTERS, B.Sc.

(*Read at the Meeting, April 2, 1919.*)

DURING recent years vessels made of fireproofed pottery-ware have been extensively introduced for culinary purposes, and are usually regarded as being more hygienic than metallic vessels; but although it is well known that pottery glazes frequently contain lead, the possibility of food cooked in such vessels becoming contaminated with lead does not seem to have been sufficiently considered.

In Germany, by an enactment of June, 1887, the sale of vessels for culinary purposes which yield any soluble lead on boiling for half an hour with a 4 per cent. solution of acetic acid is prohibited; but in this country, although regulations are laid down regarding the soluble lead in the "fritt" used for making the glaze, there does not appear to be a standard test for soluble lead in the glaze of the finished article.

Experiments made with several different types of casserole show that in some cases a considerable amount of lead can be extracted from the glaze, not only by the action of 4 per cent. acetic acid, but also by the action of more dilute solutions of organic acids—*e.g.*, 1 per cent. acetic, citric, or malic acid, such as might be used in ordinary cooking processes.

The lead extracted on boiling with 1 per cent. citric acid for thirty minutes amounted in several cases to from 2 to 4 mgrms. of lead monoxide per square decimetre of the glaze.

The results of these experiments also show that the soluble lead is by no means completely extracted by this treatment; but if the vessel is subjected to further successive treatments with the acid solution, the glaze continues to yield lead even after ten or twelve treatments.



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The amount of lead extracted by the first treatment is usually greater than that extracted by subsequent treatments, but after the first two or three treatments there is no marked decrease in the amount extracted.

The results obtained in a typical case with casserole which was filled with a 1 per cent. solution of citric acid and the solution boiled for thirty minutes were as follows (the citric acid used was tested and found to be lead free):

					Mgrms. of Lead Monoxide (PbO) per sq. dem. of the Glaze.
1st treatment	...	...	...	...	4.2
2nd "	...	..	...	...	1.6
3rd "	...	...	...	...	2.1
4th "	...	...	...	...	3.2
5th "	...	...	...	..	2.1
6th "	...	...	...	...	3.2
7th "	...	...	...	..	1.6
8th "	...	...	...	...	2.2
9th "	...	...	...	...	1.6
10th "	...	...	...	...	2.2
11th "	...	...	...	...	2.2
12th "	...	...	...	...	2.5

Total for 12 treatments 28.7 mgrms. of lead  
monoxide per sq. dem. of glaze.

These results were obtained with vessels made of pottery-ware, glazed only on the inside, which were stated to be of French make. Vessels of a similar kind, but of English make, are now being sold, and those so far examined yield considerably less lead than the French casseroles, viz. about 0.2 mgrm. per sq. dem. of the glaze, but even these, it should be noted, would fail to pass the German standard.

In the case of casseroles made of "fireproof china" with a glazed surface both inside and out, lead was not extracted, but vessels made of glazed earthenware—*e.g.*, pie-dishes, pudding-basins, etc.—in some cases yielded a trace.

KING'S COLLEGE FOR WOMEN,  
HOUSEHOLD AND SOCIAL SCIENCE DEPARTMENT.



## 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.

## GERMAN BREAD.

Two samples of German bread which I have examined may be of interest. The first sample, No. 1, was sent from Germany to a German prisoner of war in this country during last September, and sample No. 2 was bread as supplied during the early part of the same month to British officer prisoners at Graudenz camp.

	No. 1.		No. 2.	
Moisture	...	10.00	per cent.	10.00
Ash	...	2.30	"	2.60
Fat	...	0.64	"	1.05
Crude fibre	...	2.23	"	3.12
Proteins	...	9.25	"	7.68
Carbohydrates	...	75.58	"	75.55

The fibre consisted of bran tissue, and in neither bread was sawdust detected, though sample No. 2 had evidently been dusted with sawdust, a little of which had stuck to a portion of the exterior of the loaf. There is no doubt that this sawdust had been used to prevent the loaf from sticking to the oven or vessel in which it had been baked.

Both breads were very dark coloured, and, as may be imagined from the moisture figures, were very dry. Probably they had been prepared from rye with the addition of potato.

F. W. F. ARNAUD.

SESSIONS HOUSE,  
MAIDSTONE.

## NOTE ON THE RELATION BETWEEN THE KIRSCHNER REICHERT-MEISSL AND POLENSKE FIGURES IN BUTTER.

Bolton and Revis have worked out a relation between the Kirschner (K) and Polenske (P) values (ANALYST, 1912, 37, 183), and Cranfield has practically confirmed this (*ibid.*, 1915, 40, 439); the results are in each case given in a table. The formula  $P = (K - 14) \times 0.26$  gives results agreeing excellently with the mean figures, and on applying this relation to the sixty-two individual results of Cranfield, I find that thirty-two are below the figures actually found and thirty above, the differences being—

Between 0.6 and 0.7	...	...	...	in	3 cases.
" 0.5 "	0.6	...	...	"	1 "
" 0.4 "	0.5	...	...	"	5 "
" 0.3 "	0.4	...	...	"	6 "
" 0.2 "	0.3	...	...	"	7 "
" 0.1 "	0.2	...	...	"	17 "
" 0.1 "	0.0	...	...	"	23 "

It may safely be assumed that if the Polenske figure is greater than  $(K - 10) \times 0.26$ , the presence of coconut oil is established.

The relation between the Reichert-Meissl (R) and Polenske (P) figures cannot be expressed by so simple a formula; from the results of over one hundred experiments I find that this formula gives a good agreement with butters and mixtures of butter and fats other than coconut oil.

$$R \times 0.033 - 0.6155 = \log_{10} (P - 0.48).$$

In no case has the difference between the figures found and those calculated reached 0.7 c.c.

This formula may be used for calculating P' in the formula for deducing the percentage of coconut oil that I have worked out ("Dairy Chemistry," second edition, p. 322):

$$C = \frac{P - P'}{14.4} \times 100$$

where P' = mean Polenske figure calculated for a figure equal to the Reichert-Meissl figure and half the Polenske figure.

Both formulæ are approximations, and cannot be combined to express the relation between R and K.

H. D. RICHMOND.

BOOTS PURE DRUG COMPANY, LTD.,  
ISLAND STREET, NOTTINGHAM.

#### ZEISS BUTYRO-REFRACTOMETER: THE CONVERSION OF SCALE READINGS TO REFRACTIVE INDICES.

The formulæ given by C. C. Roberts (ANALYST, 1916, 41, 376) and J. F. Liverseege (*ibid.*, 1919, 49) are both more cumbersome than are necessary, and simplify down to—

$$287.7 - x = 839.4 \times \sqrt{1.5395 - [n]_D}.$$

With four-figure logarithm tables both  $x$  (scale reading) and  $[n]_D$  can rapidly be calculated from this formula. Roberts's and Liverseege's formulæ do not give quite identical results, and mine agrees with that of Roberts.

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#### NOTES ON ALCOHOL.

In a previous paper (ANALYST, 1897, 32, 154) I gave some formulæ for converting different statements of alcoholic strength. Since then Thorpe's tables have been published. Below I give the formula recalculated from his more correct data.

$$\text{Per cent.} = \frac{0.79359 v/v}{S} = \frac{w/v}{S} = \frac{0.45257 P}{S}.$$

$$v/v = \text{Per cent.} \times 1.2601 \quad S = 1.2601 \quad w/v = 0.5710 \quad P.$$

$$w/v = \text{Per cent.} \times S = 0.79359 \quad v/v = 0.45257 \quad P.$$

$$P = \text{Per cent.} \times 2.2096 \quad S = 1.753 \quad v/v = 2.2096 \quad w/v.$$

$$S = \text{specific gravity at } 60^\circ/60^\circ \text{ F.}$$

$$\text{Per cent.} = \text{grms. of absolute alcohol per 100 grms.}$$

$$v/v = \text{c.c. absolute alcohol per 100 c.c.}$$

$$w/v = \text{grms. of absolute alcohol per 100 c.c.}$$

$$P = \text{c.c. proof spirit per 100 c.c.}$$

J. F. LIVERSEEGE.

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## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

### FOOD AND DRUGS ANALYSIS.

**Experiments on the Differentiation of Cow and Buffalo Milk.** C. Todd (*Reports and Notes of the Public Health Laboratories, Cairo, 1918, 1-3.*)—Although the milk retailed in Egypt is commonly that of the Egyptian buffalo, a certain amount of cow's milk is also sold, especially in the larger towns, and as cow's milk is much poorer in fat than buffalo milk, it is necessary to fix standards for the fat content of the genuine milk from the two animals. As the result of the examination of many samples of the milk, the Department of Public Health has adopted the following standards for the two kinds of milk—namely: Solids-not-fat 8·5 per cent. for both animals, fat per cent. for buffalo 5 per cent., and for cow 3 per cent., values below these being regarded as presumptive evidence of adulteration. In the case of mixtures of the two milks trouble arises, and a test capable of indicating the presence of a comparatively small quantity of one milk in the presence of the other is desirable; the precipitin reaction is probably the most helpful. As the result of the work described, the author reaches the following conclusions: Immunisation of the cow with buffalo milk gives rise to precipitins for the milk of the buffalo and cow, and to a less extent for that of the goat. By treatment of the above immune serum with cow's milk the precipitins for the cow and goat may be removed, leaving the serum specific for buffalo milk. The original immune serum does not precipitate the normal blood-serum of either the buffalo or cow, but is hæmolytic for the red blood cells of both these animals. The antigen in the milk is soluble in dilute acetic acid, and is precipitated on neutralising the solution. Immunisation of the buffalo with cow's milk did not lead to more than traces of a precipitin. H. F. E. H.

**Composition of Egyptian Cow's Milk.** G. Hogan and A. Azadian. (*Reports and Notes of the Public Health Laboratories, Cairo, 1918, 1-6.*)—One hundred and forty-nine samples of genuine milk were analysed, the results being summarised as follows:

	Maximum.	Minimum.	Average.
Quantity of milk in litres	7	$\frac{1}{4}$	2·6
Total solids	20·05	9·25	14·63
Fat	11·0	0·6	5·44
Solids-not-fat	10·95	7·55	9·19
Immersion refractometer reading of serum at 30° C.	39·8	30·7	36·94

Eleven samples, constituting 7.4 per cent. of the total number examined, contained below 3 per cent. of fat, while ten samples (6.7 per cent. of the total) contained less than 8.5 per cent. of solids-not-fat. All but two of the samples were taken at the midday milking. Fat was determined by the Gerber method, and Ackermann's method was employed for the refractometer reading of the serum. The following results were obtained for the complete analysis of the mixed milk from the whole milking of a number of animals, 1914 and 1915 :

Number of Animals.	Specific Gravity, 15°4.	Total Solids.	Fat.	Lactose (Anhydrous).	Protein.	Ash.	Alkalinity of Ash.	Chlorine.	Non-fatty Solids (direct).	Lactose, Protein, Ash.	Immersion Refractometer Reading of Serum at 30° C.
5	1.0328	14.37	5.10	4.57	3.67	0.83	8.1	0.08	9.27	9.07	37.3
4	1.0325	13.77	4.72	4.74	3.39	0.80	8.2	0.08	9.05	8.93	37.8
5	1.0330	13.51	4.66	4.72	3.16	0.86	8.0	0.08	8.85	8.74	37.2
5	1.0310	14.97	5.99	4.60	3.37	0.82	7.8	0.07	8.98	8.79	37.0
3	1.0328	14.80	5.46	4.64	3.64	0.76	8.1	0.07	9.34	9.04	38.3
5	1.0320	17.19	7.91	4.70	3.80	0.80	7.7	0.05	9.28	9.30	37.6
5	1.0325	16.20	6.80	4.59	3.92	0.79	7.5	0.05	9.40	9.30	37.4
5	1.0325	16.00	6.18	4.76	3.89	0.77	7.7	0.05	9.82	9.42	—
5	1.0315	16.32	6.65	4.91	3.69	0.76	7.6	0.06	9.67	9.36	—

H. F. E. H.

**Composition of Egyptian Goat's Milk. G. Hogan and A. Azadian.**

(Reports and Notes of the Public Health Laboratories, Cairo, 1918, 1-6.)—The work described is a continuation of the previous abstract, the methods employed being the same. One hundred and four samples were examined, each from a different animal, with the following results :

	Maximum.	Minimum.	Mean.
Total solids	16.55	10.65	12.54
Fat	7.35	2.45	4.04
Solids-not-fat	9.95	7.6	8.50
Refractometer reading of serum at 30° C.	38.1	32.2	35.06

Six of the samples (5.77 per cent. of those examined) contained below 3 per cent. fat, while fifty-seven samples (54.8 per cent. of the total examined) contained below 8.5 per cent. solids-not-fat. It will be seen that the variation in the composition of milk from individual animals is very large, and that the proportion of non-fatty solids is unusually low. This is probably due to the fact that in Egypt a herd of goats is driven from place to place, obtaining its food by grazing along the roads, with the result that in towns the animals are habitually underfed.

H. F. E. H.

**Egyptian Lettuce Oil.** E. Griffiths-Jones. (*Reports and Notes of the Public Health Laboratories, Cairo, 1918, 1-7.*)—Lettuce oil (Arabic, *Zeit-Khass*) is obtained from the seeds of *Lactuca scariola oleifera*, a variety of prickly lettuce. When filtered and dried, the oil is of a clear golden colour, and is fluid even when kept at 0° C., no stearine being deposited even after storage for twelve months at 8 to 10° C. No characteristic colour reaction was found, and Halphen's test for cotton-seed oil and Baudouin's test for sesame oil both give negative results. When spread on a glass plate, the oil is partially dry and sticky after three days, and hard and dry after five days (temperature 28 to 30° C.).

In carrying out the Maumené thermal value test, the oil was diluted with twice its weight of pure olive oil owing to its high thermal value, the necessary correction being made for the olive oil. The "specific temperature reaction" as calculated from tables given by Lewkowitch is 205. The hexabromide test indicated the absence of linolenic acid and the presence of linoleic acid; this, together with the high iodine value and Maumené values and the visible drying property of the oil, suggests that it should be included among the semi-drying oils. With the exception of one sample obtained from the freshly gathered seeds, all the oils examined had a remarkably high acidity. The following figures were obtained from six different samples of the oil as on sale to the natives locally :

	Maximum.	Minimum.	Average.
Oil content of seeds (per cent.)	36.3	35.7	36.1
Refractive index (Abbé, 40° C.)	1.4690	1.4668	1.4682
Specific gravity (15.5/15.5° C.)	0.9334	0.9247	0.9283
Iodine value (Hübl) ... ..	136.3	120.6	127.6
Saponification value ... ..	193.0	189.3	191.1
Acidity ... ..	20.8	1.8	10.6
Reichert-Meissl number ... ..	0.3	0.0	0.13
Polenske number ... ..	0.2	0.1	0.17
Acetyl value ... ..	26.5	12.0	19.2

The unsaponifiable matter and the molecular weight of the mixed fatty acids in one sample were found to be 0.5 and 291.5 respectively.

H. F. E. H.

**Quantitative Colorimetric Estimation of Pentosans in Meal.** G. Testoni. (*Staz. sper. agri. Ital.*, 1917, 50, 97-108; through *J. Chem. Soc.*, 1919, 115, ii., 122.)—Starch, cane-sugar, maltose, and dextrose, are found on treatment with hydrochloric acid by the method of Tollens and Krueger to yield distillates giving a phloroglucide, while the hexoses, starch, and cellulose give incorrect results when estimating methyl pentosans, because when treated with dilute mineral acid they yield as an intermediate product  $\omega$ -hydroxymethylfurfuraldehyde, which gives a phloroglucide (m.p., 95° C., soluble in alcohol). It was found that pentosans could be converted into pentoses easily identifiable by colour reactions without attacking the other constituents of the meal if a different reagent from the customary 12 per cent.

hydrochloric acid be employed. The most suitable reagent is a mixture of acetic acid, 90 c.c., and concentrated hydrochloric acid (sp. gr. 1.19), 10 c.c. at 45 to 50° C. If 0.25 per cent. of phloroglucinol be added to this mixture, a red solution is formed with well-marked absorption bands when pentoses are present, starch, dextrose, and other sugars being without influence on the reaction. Complete pentosan hydrolysis is effected by forty-five minutes' heating with this reagent. H. F. E. H.

**Analyses of Old Wines.** W. I. Baragiola and O. Schupple. (*Helvetica Chim. Acta*, 1919, 11, 173-181.)—The following results were obtained on the analysis of two old Swiss wines of 1834 and 1849 vintages respectively :

	Yvorne, 1834.	Glacier, 1840.
Sp. gr. at 15° C. ... ..	0.9971	0.9925
Alcohol (grms. per litre) ... ..	62.0	105.0
Total solids (grms. per litre) ... ..	19.1	22.6
Volatile acids " " ... ..	0.8	0.6
Non-volatile acids (grms. per litre) ... ..	5.3	6.3
Ash (grms. per litre) ... ..	2.38	1.22
Sulphate, as potassium sulphate (grms. per litre) ... ..	1.50	0.25
Sulphurous acid, total (mgrms. per litre) ... ..	87.00	5.00
Total nitrogen (grms. per litre) ... ..	0.15	0.20
Glycerol " " ... ..	7.4	11.4
Tartaric acid " " ... ..	2.7	2.2
Lactic acid " " ... ..	2.8	2.0
Acetic acid " " ... ..	0.8	0.6
Tannic acid " " ... ..	0.7	0.2
Succinic acid " " ... ..	0.6	1.1
Malic acid " " ... ..	0.2	2.1

W. P. S.

**Fixed Organic Acids in Wine, particularly Lactic Acid.** G. de Astis. (*Ann. Chim. anal.*, 1918; through *Ann. Falsific.*, 1919, 12, 29-34.)—The author discusses the effect of the addition of various acids to musts on the organic acids present in wines, especially Tuscan wines. This class of wine contains tartaric acid, 1.5 to 5 grms.; succinic acid, 0.65 to 1.20 grms.; citric acid, traces; lactic acid, 0.5 to 4 grms. per litre. Malic acid, if present originally, is rapidly destroyed by bacterial action. Citric acid and sulphur dioxide are added to the wine to maintain the acidity during fermentation and storage. W. P. S.

### BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

**Method of Counting bacteria in Raw or Pasteurised Milk.** P. Allen. (*J. Infect. Dis.*, 1918, 3, 245; through *Rev. Sci. and Pract. of Agric.*, 1918, 9, 1370.)—At least twenty-four hours are required to obtain a count of bacteria in milk by the usual method of isolation on plates. A quicker result may be obtained by

adding an aqueous suspension of alumina to the milk and centrifuging the mixture, when an alumina clot is obtained containing all the bacteria free from fat and casein. The residue is spread thinly on a slide and stained with dilute methylene blue, which does not affect the alumina particles, while the bacteria can easily be counted.

H. F. E. H.

**Estimation of the Nuclein Content of Yeast.** C. A. Lubsen. (*Pharm. Weekblad.*, 1918, 55 (50), 1625-1628; through *J. Chem. Soc.*, 1919, 115, ii., 124.)—In analysing foodstuffs for nuclein content, pepsin-hydrochloric acid hydrolysis is employed (in which the nucleo-proteins are insoluble) to remove other proteins. The nucleins are then determined in the residue by estimating the phosphoric acid, which constitutes 4 to 7 per cent. of the nucleo-protein. The strength of the hydrochloric acid is of importance, for, if it be only 0.1 per cent., low results are obtained, but accurate results are yielded by 0.24 and even 0.35 per cent. acid, showing that with acid of this strength the nucleins are not further hydrolysed, as was suggested by some workers.

H. F. E. H.

**Free Lactic Acid in Sour Milk.** L. L. van Slyke and J. C. Baker. (*J. Biol. Chem.*, 1918, 35, 147-178; through *Inter. Rev. Sci. and Pract. Agric.*, 1918, 9, 1495-1496.)—Not much free lactic acid will be found in souring milk until the practical completion of the reactions of the lactic acid, first with the basic phosphates and citrates of calcium, magnesium, sodium, and potassium, and, second, with calcium caseinate. The main products of these reactions are monocalcium phosphate, free casein, and calcium lactate. From estimations of the amount of lactic acid in sour milk (1) by measurement of hydrogen-ion concentration, (2) double electrometric titration with lactic acid and hydrochloric acid, and (3) partial extraction with ether, the following conclusions have been drawn: In sour milk most of the lactic acid is in the form of lactate. Part of the free acid is in solution, and a smaller amount is adsorbed by the casein. On inoculating fresh skim-milk, pasteurised at 62° C. and cooled to 25° C., with *B. lactis acidii*, only 0.1 c.c. of free lactic acid in  $\frac{N}{10}$  solution was present in 100 c.c. after twenty hours, after which the amount increased fairly rapidly and reached 20 c.c. after forty-eight hours. In milk soured at 25° C. after pasteurisation, or treatment with *B. lactis acidii*, *B. bulgaricus*, or *Streptococcus lacticus*, the total acidity varied from 70.5 to 220 c.c. of  $\frac{N}{10}$  acid per 100 c.c.; the free lactic acid from 8.6 to 104 c.c.; the acid as lactate from 51.8 to 92 c.c.; and the hydrogen-ion concentration from 3.70 to 4.56. In milk soured under ordinary conditions the total acidity varied from 70.5 to 107.5 c.c., the free lactic acid from 13.1 to 34.5 c.c., and the hydrogen-ion concentration from 4.02 to 4.43. The casein begins to coagulate when the hydrogen-ion concentration reaches 4.64 to 4.78, and about 20 per cent. of the free lactic acid is adsorbed by the coagulated casein. The hydrogen-ion concentration remains constant during coagulation, the duration of which varies from thirty to sixty minutes. The characteristic odour and taste first perceived in souring milk is due to a volatile compound formed in the process, and not to lactic acid. There does not appear to be any relationship between the hydrogen-ion concentration or the acidity by titration and the first development of this compound.

C. A. M.



**Detection of Urobilin in Urine.** Guyot. (*Ann. Chim. anal.*, 1919, 1, 94-94.)—Ten c.c. of the urine are shaken with 5 c.c. of a 5 per cent. solution of zinc sulphate, and then, after five minutes, 5 c.c. of a 5 per cent. solution of potassium carbonate are added. The resulting zinc hydrocarbonate precipitates biliary and hæmatic pigments, and on filtering the liquid the presence of urobilin in the filtrate is indicated by the characteristic green fluorescence, the intensity of which increases with the proportion of urobilin. Most urines show a slight fluorescence, due to the presence of chromogen, which becomes partially oxidised in the course of this test. The fluorescent filtrate may be examined spectroscopically, and, when urobilin is present in large proportion, the absorption band appears at the junction of the green and blue. The fluorescence test described, however, is more sensitive than the spectroscopic method.

C. A. M.

**Autolysed Yeast as a Culture Medium for *B. coli*.** F. Dienert and A. Guillerd. (*Comptes rend.*, 1919, 168, 256-257.)—The liquid obtained by the autolysis of yeast can be used for the cultivation of *B. coli* in place of peptone, the price of which has steadily increased since 1914. About 500 grms. of pressed yeast are left for twenty-four hours at 50° C., and the resulting liquid (about 400 c.c.) is diluted with water to 2 litres, boiled for thirty minutes, neutralised, filtered, and diluted to 7.5 litres. The number of *B. coli* germs developing in this medium in twenty-four hours is greater than those developing in 3 per cent. peptone bouillon. The number is not increased by adding mineral salts to the solution. From 20 to 30 mgrms. per litre of indol are produced in twenty-four hours, and the same results are obtained on adding phenol to the liquid as in the case of peptone bouillon. Solid culture media are prepared by adding gelatin, lactose, etc., to the liquid. The composition of the autolysed liquid is fairly constant (amino acids as glycocoll 1.8, and tryptophane 0.15 per cent.). Peptones, on the other hand, vary greatly in composition, and often contain sulphurous acid, which has an influence on the characteristics of the cultivation.

C. A. M.

### ORGANIC ANALYSIS.

**Iodimetric Estimation of Acetone.** W. Marriott. (*J. Biol. Chem.*, 1918, 16, 281; through *J. Pharm. Chim.*, 1919, 19, 133-136.)—With reference to the method described by Shaffer and Marriot (*ANALYST*, 1914, 39, 184) for the estimation of acetone and  $\beta$ -hydroxybutyric acid in urine, in which use is made of Messingers' method for the estimation of acetone, the following work was done to control the accuracy of that method: A sample of acetone regenerated from the bisulphite compound was purified by distillation with permanganate and then with calcium chloride. The product was then submitted to fractional distillation, and the fraction distilling at 56° to 75° C collected. Very considerable care is required in making up and manipulating dilute aqueous solutions of acetone. The sample is weighed out in a small glass bulb of 2 to 3 c.c. capacity. The bulb is dropped into a 2-litre measuring flask and broken under water, the solution being then made up to the mark. Precautions are required to prevent loss of acetone in measuring off this dilute

solution for analysis. The flask is closed by a rubber stopper with two holes, through one of which is passed a 25 c.c. pipette. The pipette is filled by means of a rubber ball, and the measured liquid is transferred to a flask containing 500 c.c. of water, the point of the pipette being dipped below the surface of the water. To this solution 50 c.c. of  $\frac{N}{10}$  iodine and 10 c.c. of caustic soda solution at 60 grms. per 100 c.c. are added. The flask is corked, shaken, and allowed to remain for five to ten minutes; 15 c.c. of hydrochloric acid are added, and the liberated iodine is titrated with  $\frac{N}{10}$  thiosulphate. Each c.c. of  $\frac{N}{10}$  iodine consumed is equivalent to 0.000968 gm. of actone. The results are quite sufficiently accurate: for instance, acetone taken 30.62 mgrms., found 30.64 mgrms; taken 20.95, found 21.09 mgrms. Geelmuyden has stated that small quantities of acetone cannot be distilled from aqueous liquids without appreciable loss; the author has proved that, with suitable precautions, acetone can be distilled and collected quantitatively in a few minutes. Five hundred c.c. of an aqueous solution containing 33.7 mgrms. of acetone determined by the above method were placed in a Kjeldhal distillation flask of 800 c.c. capacity, with a tin condenser terminating in a glass tube dipping below the surface of 50 c.c. of water placed in a receiver. Distillation was continued for thirty minutes, but it was ascertained, by titrations made at intervals, that the whole of the acetone had distilled over after ten minutes, the distillate then containing 33.6 mgrms. of acetone by the Messinger method. The losses recorded by Geelmuyden did not occur, and it is suggested that that author did not have the end of the condenser dipping below the water in the receiver.

J. F. B.

**Solubilities, Separation, and Purification of Anthracene, Carbazol, and Phenanthrene.** J. M. Clark. (*J. Ind. and Eng. Chem.*, 1919, **11**, 204-209.)—A review of the method obtaining the "green salts" from crude coal-tar is given along with representative analyses of tars and oils and the effect of different tars and methods of distillation on the oils. The relative solubility of anthracene, carbazol, and phenanthrene in fourteen different solvents and at five different temperatures is shown. Procedures are described whereby anthracene and carbazol are obtained from 80 to 90 per cent. in purity by means of selected solvents and the proper control of temperatures. The solvents used are crude coal-tar naphtha and light coal-tar bases. A method for the preparation of pure anthracene is shown whereby the phenanthrene is removed by crude coal-tar solvent naphtha and the carbazol by fusion with a mixture of sodium and potassium hydroxides. The sublimed anthracene is then crystallised from pure benzol. A method for the preparation of pure carbazol is described whereby the phenanthrene is removed by crude coal-tar solvent naphtha and the anthracenes by the formation of a sulphonic derivative which is formed by the action of 98 per cent. sulphuric acid in the cold, and which derivative is soluble in water. The non-sulphonated carbazol is filtered and purified by sublimation. A method for the preparation of pure phenanthrene is described whereby the phenanthrene is separated from the anthracene and carbazol by dissolving in crude coal-tar solvent naphtha, boiled with animal charcoal and crystallised from 95 per cent. ethyl alcohol. The effect of different alkalis as agents for the removal of carbazol

is tabulated. A table is given showing the effect of different quantities of 98 per cent. sulphuric acid and water as agents for the removal of anthracene from carbazol.

G. C. J.

**Testing Natural Gas for Gasoline Content.** G. G. Oberfell, S. D. Shinkle, and S. B. Meserve. (*J. Ind. and Eng. Chem.*, 1919, **11**, 197-200.)—The principle of the method recommended consists in absorbing the vapours in a solid absorbing medium such as charcoal, and subsequently recovering the gasoline by distillation. Apparatus for carrying out the test is described and illustrated in detail. The absorption apparatus is portable, so that the vapours from a measured volume of natural gas can be absorbed in charcoal in the field, and the charcoal sent to the laboratory for distillation.

G. C. J.

**Estimation of the Methoxyl Group.** J. T. Hewitt and W. J. Jones. (*J. Chem. Soc.*, 1919, **115**, 193-198.)—In attempting to shorten the Zeisel process, the authors replace the alcoholic silver nitrate by pyridine, then estimate the pyridinium methyl iodide formed by diluting directly with water, acidifying with nitric acid, and adding a known amount of silver nitrate, the excess being then determined by thiocyanate according to Volhardt's method. The hydriodic acid required is prepared by saturating an aqueous suspension of iodine with hydrogen sulphide, distilling the resulting solution, and collecting the fraction which boils between 123 and 127° C. (D. 1·7) for use. The pyridine used need not be completely freed from picoline, the fraction of the purified bases obtained from the commercial material distilling between 114° and 117° C. being collected for use. The apparatus employed consists of the usual CO<sub>2</sub> generator, decomposition flask heated in a glycerol bath to 130° C., and rectifying column. The CO<sub>2</sub> carrying the methyl iodide vapour is passed through two test-tubes in series, each containing 10 c.c. of pyridine. A suitable weight of the substance to be analysed is taken, and 20 c.c. of the hydriodic acid are added. After an hour the contents of the test-tubes are washed into a graduated flask, and the iodide estimated as already indicated. The yellow coloration which early develops in the pyridine and vanishes on dilution is without significance, as it is not due to free iodine finding its way into the pyridine; if, however, it should persist after dilution, it should be discharged with a little thiosulphate. The results of many analyses are recorded, which show the accuracy of the method when employed upon brucine hydrate, methyl alcohol, methyl oxalate, alcohol, and salicylates respectively; but unsatisfactory results were obtained with a sample of methyl benzoate and one of hydrated quinine sulphate. The method has many advantages when used for the products of wood distillation or other mixtures containing methyl alcohol, which hitherto has usually been estimated in these products by conversion into methyl iodide and measurement of the volume of the latter compound, but time may be saved and greater accuracy secured by combining the methyl iodide with a tertiary base and estimating the iodine volumetrically.

A suitable amount (see below) of the liquid to be analysed is heated with 20 c.c. of hydriodic acid (D. 1·7) for one hour. The contents of the test-tubes are then completely washed into a graduated flask and made up with water to 100 c.c. An

aliquot portion (see below) of the diluted solution is introduced into a glass-stoppered bottle of 250 c.c. capacity, 70 c.c. of water are added, and then, in order, 25 c.c. of  $\frac{N}{10}$  silver nitrate solution and 30 c.c. of approximately  $\frac{N}{10}$  nitric acid. The bottle is well shaken for five minutes, and 5 c.c. of concentrated ferric alum indicator are added.  $\frac{N}{10}$  thiocyanate solution is now run in until further addition of one drop imparts a permanent orange colour to the liquid. Suitable amounts of liquids to be taken for analysis are given below.

*a* represents the volume of material to be operated on, and its dilution when necessary. *b* gives the volume of the diluted aqueous pyridine solution, obtained as described above, to be actually used in a titration. *c* is the formula to be used, giving the weight in grms. of methyl alcohol in 100 c.c. of the liquor analysed, where *t* is the number of c.c. of  $\frac{N}{10}$  thiocyanate solution used in the titration.

*Pyroligneous Acid.*—(a) Take 5 c.c. of the original liquor; (b) 40 c.c.; (c)  $0.16(25 - t)$ .

*Crude Wood Naphtha.*—(a) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of the diluted solution for distillation with hydriodic acid; (b) 40 c.c.; (c)  $1.6(25 - t)$ .

*Methyl Alcohol and Mixtures of the Alcohol with Acetone.*—(a) Take 10 c.c., dilute to 100 c.c. with water, and use 5 c.c. of this diluted solution for the estimation; (b) 20 c.c.; (c)  $3.2(25 - t)$ .

Artificial mixtures containing methyl alcohol and other products of wood distillation were made up and analysed by the method described, the results on the average being about 1 per cent. low, and Stritar and Zeidler (ANALYST, 1904, 29, 313) found that the maximum amount of methyl iodide obtainable from pure methyl alcohol in a Zeisel estimation corresponded to a 99 per cent. yield; while they also observed that the other constituents of wood distillates—acetone, formaldehyde, and acetaldehyde—give little or no methyl iodide on treatment with hydriodic acid. Methyl acetate gives one equivalent of methyl iodide, and methylal and dimethylacetal each give two. Guaiacol and other methyl derivatives of the phenols yield their equivalent of methyl iodide, but guaiacol may be eliminated from aqueous solutions of crude wood spirit by shaking with animal charcoal. The present method gives the total methyl alcohol, including both the free alcohol and that combined as methyl acetate; if desired, the ester may be determined by quantitative hydrolysis.

H. F. E. H.

**Estimation of Nitro Groups in Organic Compounds by means of Stannous Chloride.** J. G. F. Druce. (*Chem. News*, 1919, 118, 133.)—The reduction of aromatic nitro-compounds by stannous chloride in hydrochloric acid solution proceeds quantitatively, and has been used for the estimation of these compounds. The modification of this method employed by the author has given very satisfactory results in a number of cases. The procedure is as follows: A weighed quantity (0.2-0.6 gm.) of the nitro-compound is placed in an Erlenmeyer flask of 200 c.c. capacity, and about 30 c.c. of alcohol are added. The flask is connected with an apparatus generating carbon dioxide, and a slow stream of the gas is passed through the flask while the contents are warmed on the water-bath. When the air

has been displaced, 50 c.c. of stannous chloride solution of known strength, are added, and the mixture is kept warm for two hours while a slow stream of carbon dioxide is passed through continuously. The liquid is cooled, the flask is disconnected, and the excess of stannous chloride titrated back with  $\frac{N}{10}$  iodine in the presence of starch. The stannous chloride is prepared by dissolving 25 grms. of tin in 250 c.c. of strong hydrochloric acid and making up to 1,000 c.c. The solution is standardised with iodine immediately before use. Perfectly satisfactory results have been obtained with nitrobenzene, *o*-nitrotoluene, *m*-nitroaniline, *p*-nitroaniline, *m*-dinitrobenzene, and *p*-nitrotoluene.

J. F. B.

**New Reaction of Paraffin Hydrocarbons.** E. V. Lynn. (*J. Amer. Chem. Soc.*, 1919, 41, 368-370.)—During the course of some experiments with nitrosyl chloride it was noticed that a saturated solution of this gas in normal heptane remained unchanged when kept in a dark place, but in sunlight the reddish-brown colour of the solution changed gradually to blue, and ammonium chloride was precipitated; the blue colour then disappeared, and the resulting turbid liquid deposited a yellow oil; at the same time hydrogen chloride containing a little nitric oxide was evolved. The process was repeated until 50 grms. of the oil had been collected. The oil had a very fragrant odour, was soluble in alcohol, and examination showed it to consist mainly of a mixture of the three ketones from heptane (methylamyl, dipropyl, and ethylbutyl ketones), dipropyl ketone predominating. It was found that petroleum spirit, b.-pt. 45° to 70° C., gave a similar reaction with nitrosyl chloride, and it appears that the latter will prove to be a useful reagent in the study of saturated chain compounds, and also of aromatic compounds, etc.

W. P. S.

**Isolation and Examination of the Textile in Rubber-Proofed Cotton Fabrics.** B. D. Porritt. (*J. Soc. Chem. Ind.*, 1919, 38, 50-52 T.) The removal of the whole of the proofing from vulcanised and mineralised rubber-proofed fabrics is almost impossible by mechanical means. Solvents of high boiling-point will generally effect the desired result, but when very high temperatures are employed the cellulose is obviously damaged. A useful preliminary attack on the proofing composition is obtained by steeping in carbon bisulphide or extracting with this solvent in a Soxhlet apparatus. After this preparation the author recommends that the sample be heated for about an hour at 160° C. in a petroleum "white spirit" having a sp. gr. at 15.5°/15.5° C. = 0.7798, and a distillation range such that 48 per cent. distils at 170° C. and the whole at 225° C. Comparisons of the original and stripped fabrics according to their weight per square yard showed that in the case of "pure" coatings free from mineral matters the results were very satisfactory. A slight shrinkage in the width of the cloth takes place as the result of proofing, so that the weights of the stripped fabric may show a slightly heavier cloth than the original actually employed. On the other hand, fabrics are sometimes coated in the grey condition containing size, etc., in the warps, which is lost during the process of stripping; thus the stripped fabric may be slightly lighter than the original. The estimations are made in terms of dry cloth, and the weights are calculated back in terms of air-

dry material by applying the re-gain factor for moisture of 8.5 per cent. When mineral pigments, lamp-black, rubber substitutes, etc., are present, considerable variation in the treatment for stripping must be made. "Substitutes" require a subsequent treatment with N/1 alcoholic caustic soda for their complete elimination, and this is followed by boiling with dilute sodium carbonate and then treating with dilute acetic acid for removing basic matters of the ash. In some cases this may be repeated or varied by additional treatments with aqueous 2 N caustic soda and with tartaric acid solution. The completeness of the stripping is controlled by finally incinerating and estimating the ash. As a rule it is possible to obtain results sufficiently accurate for technical purposes with samples 3 inches square, although, on account of the unavoidable variability of textile fabrics, there is no guarantee that an accurate estimation of a small sample of the fabric really represents the average constitution of the whole piece. The results will tend to be less accurate the more severe and numerous the treatments with alkaline solutions necessary to render the mineral matters soluble in dilute acids. Certain mineral sulphides are very obstinate, and in some cases it is necessary to determine the cellulose by combustion after removing all the organic constituents.

J. F. B.

#### Study of Fatty Acids obtained from Varnish Oils and from Varnishes.

**W. T. Pearce.** (*J. Ind. and Eng. Chem.*, 1919, **11**, 121.)—The object of the work was to obtain information which would assist in the detection and approximate estimation of China-wood and other oils that are being substituted for linseed in oil varnishes. The linseed oil used had been boiled two hours at 200° C. with oxides of lead and manganese. The acid mixtures were in most cases obtained by making up mixtures of the desired oils, saponifying with alcoholic potash, extracting the liberated acids with ether, and drying the solvent-free acids at 110° C. The refractive index of the fatty acids gives a good measure of the percentage of China-wood oil, advancing from 1.4666 at 20° C. for pure linseed oil to 1.4707 for oil with 5 per cent. China-wood oil, 1.4775 with 10 per cent., 1.4824 with 20 per cent., and 1.4895 with 50 per cent. Where the acids come from varnishes, however, the values are not in good agreement.

The jelly test, as described by Boughton (*U.S. Bureau of Standards, Technical Paper 65*), gives useful results, but the author uses the fatty acids instead of the oils, increases the time of heating to two hours and uses 5 grms. Mixtures of soya bean and China-wood oils and cottonseed and China-wood oils give just as good results as linseed and China-wood oils, while mixtures of linseed and soya bean oils and linseed and cottonseed oils give no jelly. Menhaden oil (100 per cent.) gives a small brown residue which in no way resembles China-wood jelly. Whilst China-wood oil gives 1 inch of jelly in a 6 inch by  $\frac{5}{8}$  inch test-tube, a mixture of 50 per cent. China-wood oil and 50 per cent. linseed oil gives  $\frac{1}{2}$  inch, and when the percentage of China-wood oil falls to 33 per cent., 20 per cent., 10 per cent., and 5 per cent., the jelly formed is  $\frac{1}{4}$  inch,  $\frac{1}{8}$  inch, a very small amount, and nil respectively. China-wood and menhaden oils in the ratio 1 : 1 give  $\frac{1}{4}$  inch, and in the ratio 1 : 4 a very small amount. China-wood, menhaden, and linseed oils in the ratio 4 : 3 : 3 give  $\frac{1}{3}$  inch, and China-wood, soya, and menhaden oils in the ratio 1 : 2 : 2 give  $\frac{1}{8}$  inch. Fatty acids from a copal and rosin varnish made with China-wood, menhaden, and linseed oils in the ratio

1 : 2 : 2 gave  $\frac{1}{4}$  inch jelly, whilst a varnish containing rosin and China-wood oil alone behaved like straight China-wood oil, and one containing copal and linseed gave a negative result.

The physical characteristics of some mixtures of fatty acids are given. Those from China-wood and linseed oils in the ratio 1 : 1 are largely solid and possess a characteristic odour, whilst the reduction of the proportion of China-wood oil to 1 : 4 leads to the disappearance of the odour and most of the solids. Mixtures of China-wood oil with soya or cottonseed oils behave similarly. G. C. J.

**Methods of Varnish Analysis. W. T. Pearce.** (*J. Ind. and Eng. Chem.*, 1919, 11, 200-201.)—The author opens with the statement that “it is generally agreed that the following of any of the published methods will give results that . . . do not represent either the quantities or qualities of the materials used. . . . This opinion needs to be fully investigated.” As a result of experiments described in the paper it is shown that Boughton’s method for the separation and estimation of resins and oils, although long and tedious, does give the actual values within 3 per cent. Neither Darner’s nor Twitchell’s method can be relied on. Rosin can probably be estimated within 1 per cent. when 20 per cent. is present, or within 0.3 per cent. when 5 per cent. or less is present. For the estimation of rosin the author uses McIlhiney’s method, substituting Wolff’s esterification method for Twitchell’s. The experiments were made on varnishes of known composition, made by the author, and their preparation and the manner of calculating the final composition are described in detail. The oils used included linseed, China-wood, menhaden and soya-bean oils; the resins included Sierra Leone copal, East India copal, and kanni, whilst turpentine and benzine were used as thinners, and driers, the composition of which are not stated, were also used. G. C. J.

## INORGANIC ANALYSIS.

**Arsenious Oxide as a Standard Substance in Iodimetry. R. M. Chapin.** (*J. Amer. Chem. Soc.*, 1919, 41, 351-358.)—Pure arsenious oxide is recommended for standardising volumetric iodine solutions. A standard arsenious oxide solution may be prepared by dissolving a weighed portion of the substance in dilute sulphuric acid; complete solution is effected by boiling the mixture in a flask. The solution is then diluted to a definite volume. There is no loss of arsenious acid by volatilisation during the boiling. For the titration of iodine the latter is dissolved in potassium iodide solution, and an excess of a solution containing 8 per cent. of crystallised borax and 4 per cent. of boric acid is added before the arsenious oxide solution is introduced. W. P. S.

**Sensitive Reaction for Copper and its Application to the Analysis of Soils and Plant Ashes. L. Maquenne and E. Demoussy.** (*Comptes rend.*, 1919, 168, 489-492.)—A more sensitive reaction than the ordinary ferrocyanide reaction is a reaction given by ferrocyanide in the presence of zinc. It is most intense when the ratio of zinc to copper is of the order of 5 : 1. With moderate

quantities of copper present, the first appearance is the familiar coloration due to ferrocyanide of copper, but this quickly gives place to a blue colour, and on long standing or on centrifuging to a dark blue precipitate. If the concentration of copper be less than 1 in 200,000, the ordinary ferrocyanide reaction will not be seen in so small a quantity as 2 c.c. of the solution, but within fifteen minutes the blue colour will develop if the concentration is even as low as 1 in 1,000,000. Plant ashes (0.1 grm.) are boiled for twenty minutes with a few drops of nitric acid and 1.5 c.c. of 5 per cent. sulphuric acid, adding water from time to time to maintain the volume. The solution is washed into a small tube (70 mm. by 8 mm.), centrifuged to throw down silica and calcium sulphate, and electrolysed for twelve hours, using an electrode 10 mm. by 2 mm. and a current of 7 milliampères. The copper, which may or may not be visible, is dissolved from the cathode with 3 drops of hot nitric acid, the cathode washed with water, and the solution evaporated to dryness and the residue ignited. The residue is taken up in 3 drops of hydrochloric acid, and the solution washed into another centrifuge tube of the dimensions previously given. The volume should not exceed 2 c.c. Two drops of 1 per cent. zinc sulphate solution and one drop of a freshly prepared 10 per cent. solution of potassium ferrocyanide are then added. After the development of the blue colour the tube is centrifuged, and the colour of the precipitate compared with that of standards prepared in a similar manner. A variety of farm seeds examined in this way all showed quantities of copper of the order of 5 mgrm. per kgrm. Soils showed from 2 to 30 mgrm. per kgrm. Of such soils it is necessary to start with about 5 grms. of material.

G. C. J.

**Solubility of Plant Ash in Weak Organic Acids.** M. Sirot and G. Joret. (*Ann. Chim. anal.*, 1919, 1, 80-85.)—The solubility of the principal constituents of plant ash in Wagner's reagent (2 per cent. citric acid), and in equivalent solutions of malic, tartaric, lactic, acetic, and oxalic acids was determined, ash of different degrees of fineness and of known composition being treated for thirty minutes with the cold solutions. It was found that the solubility of the phosphoric acid varied from 25 to nearly 100 per cent. according to the fineness of the ash. The calcium salts dissolved readily in the dilute acids (excepting oxalic acid), the lowest results (46.2 to 51.7 per cent.) being obtained with tartaric acid, and the highest (79.9 to 89.2 per cent.) with malic acid. The solubility of silica in the fine ash was high (95 to 100 per cent.) in citric, malic, and lactic acids, up to 66 per cent. in tartaric acid, and from 20 to 31.7 per cent. in oxalic acid. In general, the larger the amount of soluble phosphoric acid, the greater was the proportion of soluble silica. From 10.8 to 41.4 per cent. of the iron dissolved, citric acid dissolving the most and tartaric acid the least. Up to 40 per cent. of the total manganese was dissolved by citric acid, whilst from 8.9 to 20.9 per cent., according to the fineness of the ash, was dissolved by tartaric acid. Malic acid dissolved from 23.7 to 67.6 per cent. of the magnesium, citric acid 15.3 to 32.8 per cent., and tartaric acid 3.1 to 8.6 per cent. Malic and citric acids dissolved 47.9 per cent. of the total sulphur, whilst acetic acid dissolved from 26.8 to 33.3 per cent.

C. A. M.



**Estimation of Iron by Permanganate in Presence of Hydrochloric Acid.** R. Schwarz and B. Rolfes. (*Chem. Zeit.*, 1919, **43**, 51.)—Although iron can be accurately estimated, even in presence of much hydrochloric acid, by titration with permanganate, hitherto no means were known of wholly preventing the oxidation of hydrochloric acid. Conditions were known under which the extent of the oxidation could be kept very small and constant (*cf.* ANALYST, 1909, **34**, 306). In the present paper it is shown that the oxidation of the hydrochloric acid may be wholly prevented. The method consists in the addition to the solution of a small quantity of sodium silicate solution in addition to the usual quantity of Reinhardt's manganese phosphate mixture. Commercial water-glass is diluted to a gravity of about 1.17, when it contains about 10 per cent. of silica, and 5 c.c. of this solution are added to each assay. It is important that the addition be made very shortly before the titration, as it is the silicic acid which exercises the protective influence; the gel has none. G. C. J.

**Estimation of Lead in Lead Salts; Criticism of the B.P. Method.** R. L. Morris. (*Chemist and Druggist*, 1919, **91**, 242-244.)—The British Pharmacopœia, 1914, describes lead acetate of the Pharmacopœia as containing not less than 99.5 per cent. crystallised lead acetate, and gives the following directions for its assay:

“0.5 gm. is dissolved in water acidulated with acetic acid, and the solution precipitated by excess of  $\frac{N}{V}$  oxalic acid; the precipitate is washed and transferred to a flask, decomposed with excess of dilute sulphuric acid, the mixture heated to 60° C. and titrated with  $\frac{N}{10}$  permanganate, of which 26.2 c.c. should be required as a minimum.” (26.2 c.c. corresponds to 99.35 per cent.)

Whilst the method gives accurate results if the precipitation be made in a solution containing 50 per cent. of acetic acid, and perhaps in 25 per cent., the author shows that only 99.3 per cent. of the lead present will be precipitated if the concentration of acid be as low as 5 per cent., and the analyst directed to use “water acidulated with acetic acid” might quite reasonably add much less than this. In average hands, therefore, the B.P. method may be expected to show less than 99.35 per cent. even in a sample of 100 per cent. purity. Moreover, the B.P. merely specifies an excess of oxalic acid, whereas it has been shown by Ward (*Amer. J. Sci.*, 1906 [4], **33**, 334) that at least 2 grms. of the hydrated acid per 100 c.c. of solution should be present.

Not only is the B.P. test likely to underestimate the lead in pure lead salts, but it may overestimate it in impure ones, since so many oxalates are insoluble in dilute acetic acid and soluble in hot, dilute sulphuric acid. The author expresses the opinion that it is scarcely necessary to include in the B.P. a method for the estimation of lead in lead salts. Limit tests for impurities (as for analytical reagents) should meet all requirements; but if an estimation of lead is prescribed, then the method should be improved on the lines suggested, and an upper limit, say 103 or 104 per cent., ought to be given to fix a limit for efflorescence. G. C. J.

**Electrolytic Estimation of Metals without the Use of an External Current.** M. Francois. (*Ann. Falsific.*, 1919, **12**, 7-11.)—A simple, self-contained

electrolytic cell for the quantitative deposition of certain metals may be made by placing a strip of nickel across the top of a platinum crucible and suspending a zinc rod, 5 mm. in diameter, from the strip. The zinc rod is of such length that it reaches nearly to the bottom of the crucible; it must be amalgamated twenty-four hours before being used, and during use it is covered with a filter-paper jacket, which is tied on with cotton thread. For the estimation of silver or gold, 0.2 gm. of the salt is placed in the crucible, dissolved in 2 c.c. of water and 9 c.c. of 10 per cent. potassium cyanide solution, 5 c.c. of potassium hydroxide solution (sp. gr. 1.332), and 2 c.c. of ammonia, are added. In the case of mercury, an acid electrolyte is used; about 0.5 gm. of the salt is mixed in the crucible with 0.5 gm. of potassium iodide (0.1 gm. of iodine is also added if a mercurous salt is under examination), and 20 c.c. of 10 per cent. sulphuric acid are added. The time required for the deposition of silver, gold, or mercury is twenty-four hours; with the quantities mentioned the amount of metal not recovered is 1 or 2 mgrms. W. P. S.

**Lead in Pharmaceutical Zinc Oxide.** W. D. Collins and W. F. Clarke. (*J. Ind. and Eng. Chem.*, 1919, **11**, 138-139.)—For a short time after the beginning of the war, it was not possible to procure zinc oxide in the United States which complied with the U.S. Pharmacopœia as regards relative freedom from lead. The U.S.P. test detects 0.1 per cent. with certainty, and fails to detect 0.05 per cent. In view of the unsatisfactory nature of the zinc oxide on the market, the matter was brought to the attention of the U.S. Geological Survey, which was able to indicate a mine, situate within the United States, which was free from lead minerals. From this mine and from electrolytic zinc from other sources, zinc oxide with far less than 0.05 per cent. of lead is to-day being manufactured in the United States by at least four firms. G. C. J.

**Accurate Estimation of Soil Nitrates by Phenol Disulphonic Acid Method.** H. A. Noyes. (*J. Ind. and Eng. Chem.*, 1919, **11**, 213-218.)—Experiments are described which show that the phenol disulphonic acid method, when carried out as recommended by the author, is adapted to the accurate estimation of soil nitrates. Nitrates are completely extracted from soils when these are shaken with 4 parts of water, and nitrates added to soils are completely recovered in addition to those present in the soil. Chlorides have no effect, even when 100 times as much chloride as nitrate is present, provided the precautions outlined below are taken. Clear soil extracts can be obtained by the proper use of filter-paper—namely, by getting as much as possible of the soil on to the filter and returning the first runnings. Calcium hydroxide has been found the best precipitant of coloured organic matter, and also removes iron and other interfering inorganic substances. The use of small aliquot portions of the extracts makes it easier to keep the temperature of reaction low, and thus restricts the loss of nitrogen by interaction of nitrate, chlorides, and sulphuric acid. The details of the method recommended are as follows:

A weighed quantity of the soil (50 grms.) is shaken for a minute with a measured volume (200 c.c.) of water. The mixture is shaken again after half an hour, and again after a further half-hour. It is then transferred to a 24 cm. filter, getting as much

as possible of the soil on to the filter. The first runnings are refiltered through the bed of soil until a bright filtrate results. If the soil gives a coloured extract or contains soluble iron, 5 grms. of calcium hydroxide are added to the soil just before the 200 c.c. of water is poured on to it. When 50 c.c. of clear filtrate have been collected, 5 c.c. are measured into a 7 cm. dish and evaporated to dryness on the steam-bath. A measured portion (5 c.c.) of standard potassium nitrate containing 0.1 mgrm. of nitrogen per c.c. is evaporated simultaneously. When the dishes are cool, 1 c.c. of the phenol disulphonic acid solution of Chamot, Pratt, and Redfield (*ANALYST*, 1911, **36**, 244) is added drop by drop in a ring about the dish, and these drops are allowed to spread down over the dry residue. The dishes are rotated to make sure that all the residue has come in contact with the acid, and are then allowed to stand for fifteen minutes. Then, down the side of each dish, so as not to have the water and acid mix too rapidly, 15 c.c. of cold water are added. Dilute (5 per cent.) ammonium hydroxide, from a wash-bottle with fine jet, is next played over and through the solution in such a way as to prevent violent local heat reactions, ceasing the addition when the yellow colour is permanent. The author makes the colour comparisons with a Schreiner colorimeter (*J. Am. Chem. Soc.*, 1905, **27**, 1192). Individual readings never differ by more than 3 per cent. from the mean of a number, whilst the maximum error of the method, with the maximum ratio of chlorine to nitrogen likely to be encountered (150 : 1), does not exceed 5 per cent.

G. C. J.

**Detection and Estimation of Ozone.** L. Benoist. (*Comptes rend.*, 1919, **168**, 612-615.)—A method of detecting and estimating ozone has been based upon its power of bleaching the colour and destroying the fluorescence of very dilute solutions of fluorescein. Oxidising agents such as very dilute nitric acid or potassium ferrocyanide do not attack fluorescein, nor do the traces of nitrous vapours in the atmosphere destroy the fluorescence. Chlorine readily attacks the reagent, but in dilute ( $10^{-3}$ ) solution does not affect a ( $10^{-6}$ ) solution of fluorescein, whilst carbon dioxide has only an appreciable influence when present in the proportion of twenty to thirty times that of the fluorescein. Two molecules of ozone appear to react with one of fluorescein. In applying the test a Nernst lamp is placed in a box with blackened walls, in the lid of which are two adjacent openings, one of which supports a tube containing the fluorescein solution, and the other a similar tube containing an equal quantity of distilled water as a check. The action of  $10^{-9}$  grms. of ozone in destroying the fluorescence of 3 c.c. of a  $10^{-9}$  solution of fluorescein can be plainly seen in the dark room, and the test is thus capable of detecting traces of ozone insufficient to turn starch-iodide paper blue. By using a graduated series of standard solutions of fluorescein for comparison, the amount destroyed in the given tube under examination may be found, and the test made quantitative.

C. A. M.

**Solvent Action of Dilute Citric and Nitric Acids on Rock Phosphate.** J. A. Stenius. (*J. Ind. and Eng. Chem.*, 1919, **11**, 224-227.)—The author has been engaged in experiments the object of which was to ascertain under what conditions the process of sulphur oxidation, termed "sulphofication," will bring about an-

increase in the availability of phosphorus in rock phosphate. In this connection it was important to secure a method by which a trustworthy index of the changes in availability of the phosphorus compounds in rock phosphate and soil mixtures attributable to sulphofication could be obtained. In view of the unsatisfactory behaviour of neutral ammonium citrate solution, attempts were made to discover a solvent which would serve better as a solvent of "available" phosphorus. No success attended these efforts, nitric acid as weak as 0.015 per cent. dissolving as much as two-thirds of the total phosphate in rock phosphate, whilst citric acid failed for other reasons. A 0.2 per cent. solution of citric acid has almost the same solvent action on rock phosphate as has neutral ammonium citrate, when 3 grms. of the phosphate are treated with 200 c.c. of the solution, and the citric acid solution is very much easier to prepare than neutral citrate solution. Enormously higher results (up to twenty times as much) are obtained if a smaller quantity of phosphate or larger volume of solution is taken for the test, however, and, although no error from this source would arise in a standardised test, the fact suggests a grave doubt whether the results of the test have any definite relation to the true "availability" of the phosphorus extracted. Moreover, the solvent power of dilute citric acid is profoundly modified by any calcium carbonate which may be present, and is not even approximately corrected by adding additional citric acid exactly equivalent to the calcium carbonate known to be present. The author was, therefore, thrown back on the neutral ammonium citrate method, which, while it cannot be regarded as an absolute measure of available phosphorus, probably gives as trustworthy an indication of changes of availability due to sulphofication and other processes as any solvent can be expected to furnish. It is necessary, however, that two determinations be made, one at the beginning and one at the end of the experiment, and absolutely uniform conditions be maintained in both instances.

G. C. J.

**Estimation of Phosphorus in Vanadium Steels, Ferrovandium, Non-Vandium Steels, and Pig Iron.** C. M. Johnson. (*J. Ind. and Eng. Chem.* 1919, 11, 113-116.)—Of vanadium steels, 1.63 grms. are dissolved in 45 c.c. dilute nitric acid (sp. gr. 1.13) over a low flame. When the solution is clear and brown fumes have disappeared, 3 c.c. of 5 per cent. permanganate are added, the solution is boiled for three minutes, 3 c.c. of approximately  $\frac{N}{1}$  ferrous sulphate are added, the solution is boiled until brown fumes have disappeared, 40 c.c. concentrated nitric acid are added, the mixture is heated to boiling, 50 c.c. of a specially prepared molybdate solution are added, the mixture is stirred vigorously for a minute, and left to stand overnight. The molybdate solution, which keeps indefinitely, is prepared as follows: A mixture of 55 grms. ammonium molybdate, 50 grms. ammonium nitrate, and 40 c.c. dilute ammonia (sp. gr. 0.95), is diluted to 700 c.c., heated for thirty minutes until all salts are in solution, diluted to 1,000 c.c., let stand overnight, and filtered through a double paper. The ammonium phosphomolybdate from the vanadium steel is filtered off on a 7 cm. paper with a little pulp in the apex, washing the iron out of the paper by fifteen washings with 1 per cent. nitric acid before transferring the precipitate to the filter. The precipitate is washed fifteen times with the dilute nitric acid and twenty-five times with 0.1 per cent. potassium nitrate

solution, or until the washings are no longer acid. The precipitate and paper are treated in a beaker with a measured volume of standard sodium hydroxide solution, and the excess of the latter titrated with standard nitric acid, using phenolphthalein as indicator.

Of ferrovanadium, 1 gm. is digested in a porcelain dish with 30 c.c. hydrochloric acid and 30 c.c. nitric acid for about an hour, after which a further 100 c.c. nitric acid are added and the solution evaporated to dryness. The residue is baked at 750° C. in an electric muffle. The oxides are dissolved in 35 c.c. hydrochloric acid the solution is evaporated to 10 c.c., 50 c.c. nitric acid are added, the solution again evaporated to 10 c.c., and 10 c.c. more nitric acid added. The solution is heated a short time with cover-glass on, then filtered through a platinum Gooch crucible with a pad of asbestos, using suction. The filter is washed fifteen times with a solution made by mixing 200 c.c. nitric acid, 100 c.c. water, and 20 grms. ferric nitrate. The filtrate is concentrated to 10 c.c. and a second crop of vanadium "rust" filtered off. A third concentration to 10 c.c. should show no "rust." To the third concentration 40 c.c. nitric acid are added, the solution heated to boiling, 50 c.c. of the faintly ammoniacal ammonium molybdate are added, the mixture stirred for two minutes and filtered after an hour, finishing as above described.

The above ammoniacal solution of molybdate is recommended for use with non-vanadium steels and pig iron. The sample (1.63 grms.) is dissolved in 45 c.c. dilute nitric acid (sp. gr. 1.13). In the case of pig iron and certain chrome steels, a carbon residue must be filtered off, and the filtrate and washings concentrated to 50 c.c. The solution is oxidised with permanganate, the excess of which is destroyed by means of ferrous sulphate, as described in the first paragraph. Nitric acid (15 c.c.) is added, the solution heated to boiling, 50 c.c. of the molybdate solution are added, the mixture stirred for two minutes, allowed to stand half an hour, and the analysis completed as above described.

G. C. J.

**Reduction of Potassium Platinichloride.** Horsch. (*Comptes rend.*, 1919, 168, 167-169.)—The double chloride of potassium and platinum is washed with 80 per cent. alcohol, and then dissolved in boiling water in a tared platinum crucible. The solution is treated with 2 to 3 c.c. of alcohol and heated on a boiling water-bath. After about a minute the reduced platinum begins to deposit uniformly over the interior of the crucible, and the reduction is complete in about twenty-five minutes. The deposit is then heated for five minutes, after the addition of a few drops of alcohol, then washed with water, dried on the water-bath, strongly ignited, and weighed. This reduction with alcohol is only practicable in the case of solutions containing not more than 0.25 to 0.3 per cent.; in more concentrated solutions the reduction is slow and incomplete, and the platinum only adheres partially to the crucible. Formaldehyde also does not yield a completely adherent deposit, whilst allyl alcohol does not effect any reduction.

C. A. M.

**Estimation of Sulphur in Pyrites.** H. C. Moore. (*J. Ind. and Eng. Chem.*, 1919, 11, 45-49.)—The Allen and Bishop method is recommended. In this method the sulphur is oxidised with bromine dissolved in carbon tetrachloride and by subse-

quent heating with nitric acid, and the resulting sulphuric acid is precipitated as barium sulphate, after removal of silica and reduction of ferric salts by the addition of aluminium powder. The method yields concordant results when used by different analysts on the same sample of pyrites.

W. P. S.

#### Estimation of Sulphites and of Sulphur Dioxide in Gaseous Mixtures.

**P. Haller.** (*J. Soc. Chem. Ind.*, 1919, **38**, 52-56 T.)—The author discusses the analysis of the sulphur dioxide gases in the manufacture of sulphuric anhydride by the contact process. He prefers for the absorption liquid a solution of caustic soda rather than iodine solution. One of the principal sources of error is the oxidation of the sodium sulphite by the oxygen present in the gases and dissolved by the liquid. This oxidation is strongly influenced both by positive and negative catalysts. Positive catalysts which intensify oxidation include salts of copper and iron; negative catalysts which suppress it include substances like mannitol and glycerin. The addition of 5 per cent. by volume of glycerol to solutions of sulphite or to caustic soda solutions employed for absorbing sulphur dioxide effectively prevents the oxidation of the sulphite due to the passage of air or exposure to high temperatures, and does not interfere with the estimation of the sulphite. Consequently, the results of analyses made with the use of glycerol are consistently higher than those obtained without it. A 10 per cent. solution of caustic soda is employed for the absorption. For the estimation of the sulphite the author recommends a method described by Andrews (*ANALYST*, 1903, **28**, 306) depending on the use of potassium iodate solution in strongly acid solutions. Under these conditions the reaction proceeds according to the equation  $2\text{SO}_2 + \text{KIO}_3 + 2\text{HCl} = 2\text{SO}_3 + \text{KCl} + \text{H}_2\text{O} + \text{ICl}$ , and the end-point is marked by the complete disappearance of the free iodine liberated in the first stage of the reaction. This is recognised by the presence of a drop of chloroform to serve as an indicator during the titration. The acidity of the solution should correspond to 15 to 20 per cent. of free hydrogen chloride. The iodate solution may be standardised against potassium iodide ( $2\text{KI} = \text{KIO}_3$ ) or by absorbing pure sulphur dioxide in caustic soda solution containing glycerin under conditions adapted for ascertaining accurately the increase in weight. The solution is diluted in a measuring flask so as to contain approximately 0.1 per cent. of  $\text{SO}_2$ , 25 c.c. are added to a sufficient quantity of strong hydrochloric acid, and titrated in the presence of a globule of chloroform. Andrews suggested the use of a solution of iodine monochloride in order to prevent the loss of sulphur dioxide when the sulphite is first added to the strong hydrochloric acid. Such a precaution is, however, unnecessary, and the iodine monochloride solution is extremely unstable and difficult to control. The accuracy of the titration depends largely on the thoroughness with which the solution is shaken towards the end. The point of disappearance of the iodine from the chloroform is sharp, but on standing for an hour or two the colour returns, owing to the decomposition of the iodine monochloride into the trichloride and free iodine; this secondary reaction, however, is too slow to affect the results.

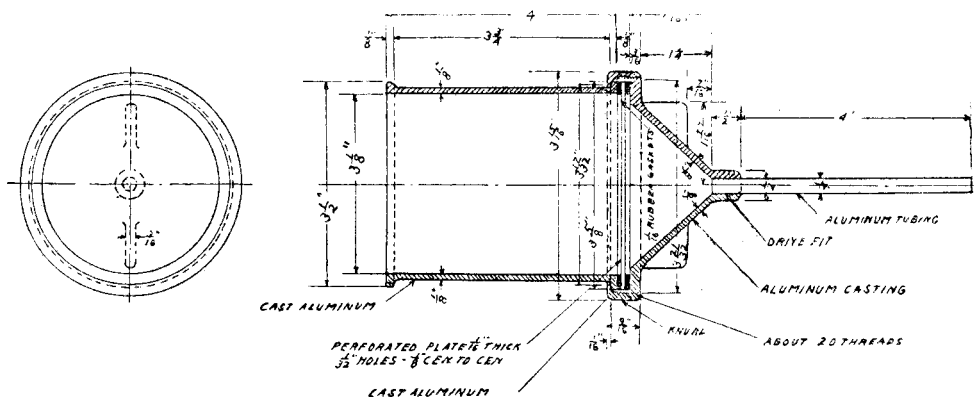
J. F. B.

**Estimation of Zirconium.** P. Nicolardot and A. Reglade. (*Comptes rend.*, 1919, 168, 348-351.)—Doubt having been cast on Hillebrand's method for the separation of zirconium from iron, aluminium, and chromium by precipitation as phosphate in presence of sulphuric acid, the authors have reinvestigated the method. They find the separation is a clean one if the concentration of sulphuric acid is not less than 20 per cent. and not much more. With 19 per cent. sulphuric acid present an appreciable quantity of iron is carried down, less acid is required to hold up chromium, whilst even 5 per cent. will hold up aluminium. The upper limit of concentration was less closely investigated. When 35 per cent. of sulphuric acid is present, about 2 per cent. of the zirconium escapes precipitation. The method consists in adding excess of ammonium phosphate solution to the acid solution of salts of zirconium, ferric iron, chromium, and aluminium, allowing to stand two hours, and filtering and washing the precipitate, which is finally ignited to pyrophosphate. The ignition should be carried out with the crucible covered at first, as the precipitate tends to decrepitate. G. C. J.

APPARATUS, ETC.

**New Reflux Condenser.** J. B. Bajda. (*J. Ind. and Eng. Chem.*, 1919, 11, 52.)—The vapours from the boiling flask pass upwards through an external side tube which extends from the stem of the condenser jacket just above the cork, closing the flask to the top of the jacket; the tube there enters the jacket, and forms a spiral in the latter. The lower end of the spiral is provided with a siphon trap which delivers the condensed liquid through the stem of the condenser into the flask. A vertical tube extends from just above the siphon through the top of the jacket. In this type of condenser the hot vapours enter the upper or relatively warmest part of the condenser. W. P. S.

**Funnel for Filtering Volatile Organic Solvents.** T. B. Aldrich. (*J. Ind. and Eng. Chem.*, 1919, 11, 139-140.)—The difficulty of filtration of volatile solvents,



owing to the fact that the paper does not adhere to the funnel as a wetted paper does, is well known. The difficulty is especially great with filters of the Buchner

type. The present invention overcomes this difficulty by clamping the filter-paper securely between two plates. The funnel is of aluminium, and consists essentially of four parts: (1) A hollow cylinder, 4 inches high and  $3\frac{1}{2}$  inches in diameter, with a small flange at the top and a heavier one at the bottom; (2) a plate  $\frac{1}{8}$  inch thick, perforated with  $\frac{1}{32}$  inch holes ( $\frac{1}{8}$  inch centre to centre) extending to within  $\frac{1}{8}$  inch of the circumference; (3) a ring  $\frac{9}{16}$  inch wide and  $\frac{1}{8}$  inch thick, threaded on the inside and milled on the outside, having a shoulder on the upper inside which engages the lower upper surface of the shoulder of the cylinder, this latter preventing the ring from passing over the lower end of the cylinder; (4) a cone-shaped lower portion with stem, having also a flange at the top  $\frac{1}{4}$  inch thick and threaded on the outside so as to mesh with the threads on the inside of the ring. The lower flange of the cylinder, the plate, and the top of the flange of the cone have approximately the same outside diameter, as must also the gasket and filter-paper to be used. The upper flange on the cylinder is merely to add strength, but the lower is essential as a shoulder of resistance for the ring when the cylinder, plate, cone, gasket, and paper are pressed together, by meshing the ring with the cone. In preparing the funnel for filtering, it is only necessary to have the lower flange of the cylinder, the filter-paper (placed on top of the plate), the perforated plate, the gasket (placed between the flange of the cone and plate), and the flange of the cone, flush with one another, pass the ring with the flange or shoulder uppermost over the top of the cone, screwing as tight as necessary to secure a perfect joint. A key made of hard wood and carrying two slots which engage two offsets shown in the drawing and plate, opposite each other on the lower part of the cone, facilitates the operation of tightening and loosening the parts.

G. C. J.

**Guttameter and its Application to the Study of Drugs and Poisons.** F. Eschbaum. (*Ber. Deut. pharm. Ges.*, 1918, **28**, 397-416; through *J. Chem. Soc.*, 1919, **115**, i., 139.)—The apparatus consists of a capillary pipette with a wide lower opening so standardised as to deliver 10 drops of water at 20° C., weighing 1.2 grms.; and this weight, when corrected by the standardisation factor of the pipette, is proportional to the surface tension of the liquid employed. It has been found by Traube and others that the toxicity of alkaloidal solutions is in direct proportion to the lowering of the surface tension of water caused by the alkaloid at standard concentration, and in this way a number of derivatives of quinine alkaloids, when arranged in the order of decreasing surface tension are found to be in accordance with their increasing toxicity. The depression of the surface tension increases with the amount of alkali present in the alkaloidal solutions, sodium carbonate being the usual alkali, employed in 0.1 per cent. solutions of the alkaloidal salt. Morphine and apomorphine behave anomalously, but when treated with ammonia in place of sodium carbonate show a depression of the surface tension due to the liberation of the alkaloid in a disperse form.

H. F. E. H.

**Permanent Marking of Glass Vessels.** J. C. Bock. (*J. Amer. Chem. Soc.*, 1919, **41**, 359-361.)—The method proposed consists in the use of a glass colour which is fused into the glass by means of an ordinary burner. The glass colour



(Green, 728 D, obtainable from Roessler and Hasslacher, New York) is mixed with a medium composed of copaiba balsam 4, clove oil 1, and lavender oil 1 part, and a steel pen is used to apply this paint to the glass. The marked part of the glass is then heated carefully by placing it against the side of the flame of a Meker burner, the heating being continued until all carbonaceous matter has been oxidised, and the marking, not the glass, begins to glow. Beakers, flasks, porcelain crucibles, etc., may be marked permanently by this process. W. P. S.



### REVIEW.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By A. W. STEWART. Third Edition. Price 14s. net. Pp. 350 + xix and one chart. Longmans, Green and Co. 1918.

This volume deals in a most interesting manner with the results of recent chemical research. In a comparatively brief space the most important developments of the science of organic chemistry are very satisfactorily treated, the effect, however, being somewhat marred by the attempt to include more than the space available permits. Owing to this unfortunate effort some few of the chapters are scanty and compare unfavourably with the excellence of the remainder of the book.

Writing admittedly in a critical spirit, the author, in the main, gives his readers an admirably balanced statement concerning the facts that have been ascertained, and carefully points out where experimental results end and purely theoretical reasoning begins, but there are places where this balance is lost.

When perusing the volume, one cannot fail to be struck with the prominence that is given to the chemical investigation of natural products, for no less than nine of the fourteen chapters are devoted to work in this branch of organic chemistry. That this should be so is fully justified by the large amount of work that has been carried out during recent years in this field and the importance of the results obtained. Moreover, despite the almost fanatical energy with which the investigation of aromatic and other synthetic compounds has been carried on in many laboratories, there is still a magnetism about the products of vital action, whether of the vegetable or animal world.

In the opening chapter the general trend of organic chemical investigation in the twentieth century is well, if briefly, surveyed. The chapters dealing with the terpenes and alkaloids are wholly excellent, whilst that treating of chlorophyll contains an admirable survey of this intricate subject. In the chapter on the anthocyanins an interesting account of the recent work on these pigments is given, but it is erroneously stated that the term anthocyanins includes all sap-soluble pigments.

One of the most interesting chapters is that which deals with theories concerning the natural synthesis of vital products, but the reader needs to be very careful to observe the extent to which speculation is carried without direct chemical evidence being available. Judgment on the value of such speculation must be left

until success or failure attends work based upon it ; one is, however, given an uneasy feeling that the general line developed in this chapter is rather too flexible in its present form, its very flexibility making experimental proof or contradiction very difficult.

An interesting account is given of the various cases of abnormal valency which have been observed in the course of recent researches, but the chapter in which the deficiencies of modern formulæ are discussed, whilst dealing with what is admittedly a problem, is open to very considerable criticism.

The book, as a whole, is well written and well produced. It should prove of great assistance to advanced students and to those taking up research in the subject, by bringing before them the value of investigation with a definite objective in view ; it is, moreover, full of ideas suggestive of work that needs to be carried out.

A. E. EVEREST.

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