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THE ANALYST.

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

An ordinary meeting of the Society was held on Wednesday evening, March 7, in the Chemical Society's Rooms, Burlington House. In the absence, through indisposition, of the President, the chair was occupied by Dr. Harold G. Colman, F.I.C., Vice-President.

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

A certificate of proposal for election to membership in favour of Mr. H. C. S. de Whalley was read for the second time.

Professor A. F. Joseph, D.Sc., A.R.C.Sc., F.I.C., was elected a member of the Society.

The following papers were read: "The Composition of Milk," by Paul S. Arup, B.Sc., A.I.C., Horace C. Huish, and H. Droop Richmond, F.I.C.; "Studies in Steam Distillation—Part IV.: Propionic, Butyric, Valeric, and Caproic Acids," by H. Droop Richmond, F.I.C.; "Studies in Steam Distillation—Part V.: The Analysis of Acetic Anhydride and Alkyl-Malonic Acids," by H. Droop Richmond, F.I.C.; "The Quantitative Estimation of Mercury in Organic Compounds," by J. E. Marsh, M.A., F.R.S., and O. G. Lye; and a "Note on Salvarsan and Neo-Salvarsan," by John Webster, F.I.C.

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ANNUAL ADDRESS OF THE PRESIDENT.

(*Delivered at the Annual General Meeting, February* 7, 1917.)

It has been the custom, at the end of each session of this Society, for your President to take stock of the previous year's work, and although I cannot hope to rival the illuminating addresses to which you have listened during the forty-two years of the Society's existence, I will do my best to record the events of a year passed during the most awful period of European history.

It could hardly have been expected that our work would not suffer when young and vigorous members of our Society are employed in devising means for destroying life rather than in helping to keep our fellow-beings alive and healthy.

On December 31, 1916, the number of our members was 448, of whom 435 were ordinary and 13 honorary. In 1915 we had 455 members, of whom 440 were ordinary and 15 honorary—that is, a reduction of 7. We have lost by death 2 honorary and 5 ordinary members.

The death of Sir William Ramsay is so profound a loss, and the obituary notice furnished by Mr. Hehner is so complete, that anything I can say in the time at my disposal would be quite inadequate.

Mr. David Howard was best known to us through his connection with the Institute of Chemistry, he having held the offices of both Treasurer and President. I have pleasant recollections of his visits to us and of the wise counsels he offered on more than one occasion.

The death of Mr. Wallis Stoddart has left a gap in the city of Bristol which will not be easily filled. He was my near neighbour, and we were always very good friends, and yet through the irony of fate we seemed to be always in opposition. Thirty-four years ago we were both candidates for the posts I now hold, and although our meetings in police and law courts were quite frequent, we were always retained by opposing litigants. He was, however, a generous opponent and a good loser. His contributions to our proceedings included:

"A Simple and Effective Fat Extraction Apparatus."

"A New Pepper Adulterant."

"The Separation and Identification of the Typhoid and Colon Bacilli."

"Somerset House and Water Analysis."

"The Incubator Test for Sewage Effluents."

"The Interpretation of Results in Water Analysis."

Messrs. E. A. Lewis and L. de Koningh had been members for some years, but had not lately taken any active part in its work. Mr. Mitchell was a comparatively new member.

During the year twenty-four papers were read. Two of these—viz., "Microscopical Methods," by Professor Greenish, and "Quantitative Microscopy," by Mr. T. E. Wallis—were very valuable when we consider the reviving position of this method for examining foods, drugs and feeding-stuffs.

Two other papers also demand serious consideration, having formed interesting additions to our knowledge of edible fats—viz.:

"Some New Oil-Seeds, derived from American Palms," by Messrs. G. T. Bray and F. L. Elliott."

"Brazilian Oil-Seeds," by Mr. E. R. Bolton and Miss Dorothy Hewer.

A paper which interests us at the present time was communicated by Messrs. Bevan and Bacon on "The Manufacture of Filter-Paper"; and this, in conjunction with the following exhibits, well illustrates the efforts made by English manufacturers to make us independent of foreign supplies:

At the March meeting the Worcester Royal Porcelain Company exhibited good specimens of porcelain laboratory ware. At the April meeting Messrs. Baird and Tatlock showed porcelain and glass ware, and Messrs. Bellingham and Stanley, of Hornsey Rise, sent for our inspection an English-made polariscope, which could well supply the needs of an analyst's laboratory.

As to our financial position, this, thanks to our Acting Treasurer, has been satisfactory. The amount received from subscriptions was £448 3s., as against £435 14s., in 1915. The expenditure has been reduced by nearly £20, chiefly due to a reduction in the expenses on postages. The ANALYST has cost less. The receipts from advertisements have nearly doubled. The cost of our journal was £131, against £195 in 1915; but our position in regard to the ANALYST is one of temporary loss, due to the production of that exceedingly useful volume, the Decennial Index, and I would again urge upon our members to lose no time in securing a copy, as by this means they will be saved a considerable amount of time and will be helping the Society financially.

My long and pleasant association with you has led me to form the opinion that analytical chemists are very sociable people, and the establishment of a Dinner Club has done much to bind us together, and has enabled us to become acquainted with each other's virtues and failings; but this advantage can only be enjoyed by members living within a short distance of the Metropolis. I therefore regret that country meetings—which were so pleasant—should have been abandoned. To me personally this has always been a matter for regret, especially when I call to memory the fact that they were discontinued at a time when I had suggested as a suitable place the ancient and historic city of Gloucester—a city where Kings were crowned, where parliaments were held, and which is one of the few places containing a garrison built nearly 2,000 years ago. I hope that when happier days return and peace once more reigns, the consideration of resuming this pleasant function will again occupy the consideration of your Council.

During the year very few legal decisions of importance have been given. Two have been reported in the ANALYST. The first of these was Haigh *v.* Aerated Bread Company. The sample in question was one of cream containing 0·34 per cent. of boric acid. The magistrates dismissed the information, but on appeal this decision was reversed. Justices Ridley, Bray, and Avory, in giving judgment stated that the magistrates had not distinguished between Sections 3 and 6; they ought to have convicted the respondents.

The next case is of far greater importance, and I think its discussion at one of our meetings would be of advantage to Public Analysts. The case to which I refer is that of Hunt *v.* Richardson. The appeal was against a decision of the Cambridge magistrates. John Hunt, the appellant, was summoned for having sold milk deficient in fat to the extent of 9 per cent., and a fine of forty shillings and costs was imposed. Against this he appealed, and the appeal was allowed by a majority of the Judges, three being in favour and two against it, and if this be allowed to stand our chances of obtaining convictions for milk deficient in fat will be very slender.

A year ago my predecessor, Mr. Chapman, introduced in a very able manner the question of training for analytical chemists. He placed before you one view of the question with which most of us seemed satisfied at the time, but it would be manifestly inconvenient to discuss the opinions forming the matter of a Presidential Address, though it is quite possible that there are phases of the subject which may modify opinions first formed, and there are other aspects of the question worthy of our consideration.

That an analytical chemist should be well trained we all agree. Whether he should be learned in ancient or modern languages would not be so generally accepted, although opinion would favour such acquirements if time permit.

Some recently proposed regulations of the Institute of Chemistry seem to imply that the worst place in which he may be trained is the laboratory of a working analyst. I refer to the proposed regulations given on page 3 of the circular issued on November 28, 1916, in which two years' training in the laboratory of a Fellow of the Institute can only be considered as equal to one year in a college laboratory.

I know that the subject is a difficult one, and I am reminded of the change which has taken place in the training of a skilled mechanic. Time was when he had to serve an apprenticeship to a master of his craft, yet now a year or two in one of those modern institutes called technical schools, and a short time in a workshop, produces a much inferior artisan. There is a growing tendency at the present time to convert our schools into workshops, to the neglect of science.

At almost every meeting of our Council some protest is made against the usurpation of the duties of the analyst by bodies supported by rates, endowments, or Government subsidies, and if our colleges be converted into institutions for the teaching and practice of technology, to the neglect of science, we shall find ourselves in a parlous state, and even the institutions themselves will decay for lack of students.

Perhaps the best method would be to devote time at the end of a teaching course to research work. I am quite convinced, after an experience extending over more than half a century, that the best place for learning analytical chemistry is an analyst's laboratory.

I crave your pardon for having introduced matter of a controversial character, and thank you for much kindness and forbearance, but most especially our ever-helpful Secretaries, our Acting Treasurer, and my predecessor, for constant help and kindness.

* * * * *

THE COMPOSITION OF MILK.

By PAUL S. ARUP, B.Sc., A.I.C., HORACE C. HUISH, and
H. DROOP RICHMOND, F.I.C.

(*Read at the Meeting, March* 7, 1917.)

The present communication deals with the results obtained in the laboratory of the Aylesbury Dairy Company during 1914, 1915, and 1916.

The monthly and yearly averages given in Table I. are based on series of 19,317, 16,118, and 14,286 samples for 1914, 1915, and 1916 respectively, referring to the milk as received from the farms. The morning and evening milks have been kept separately, and the numerical mean between the two is given.

TABLE I.—AVERAGE COMPOSITION OF MILK DURING 1914, 1915, AND 1916.

MONTH.	MORNING MILK.				EVENING MILK.				MEAN.			
	Sp. Gr.	Total Solids.	Fat.	Solids, not Fat.	Sp. Gr.	Total Solids.	Fat.	Solids, not Fat.	Sp. Gr.	Total Solids.	Fat.	Solids, not Fat.
1914.												
January..	1·0320	12·66	3·76	8·90	1·0320	12·80	3·90	8·90	1·0320	12·73	3·83	8·90
February.	1·0320	12·44	3·59	8·85	1·0319	12·60	3·72	8·88	1·0319	12·52	3·66	8·86
March ..	1·0319	12·33	3·52	8·81	1·0318	12·48	3·65	8·83	1·0319	12·41	3·59	8·82
April ..	1·0318	12·21	3·43	8·78	1·0316	12·40	3·62	8·78	1·0317	12·30	3·52	8·78
May ..	1·0323	12·12	3·26	8·86	1·0320	12·47	3·61	8·86	1·0321	12·30	3·44	8·86
June ..	1·0320	12·17	3·34	8·83	1·0315	12·47	3·70	8·77	1·0318	12·32	3·52	8·80
July ..	1·0316	12·16	3·43	8·73	1·0311	12·48	3·80	8·68	1·0314	12·32	3·62	8·70
August ..	1·0315	12·24	3·52	8·72	1·0312	12·56	3·86	8·70	1·0313	12·40	3·69	8·71
September	1·0317	12·42	3·62	8·80	1·0315	12·79	3·99	8·80	1·0316	12·60	3·80	8·80
October ..	1·0316	12·52	3·76	8·76	1·0310	12·73	4·01	8·72	1·0313	12·63	3·89	8·74
November	1·0317	12·85	3·98	8·87	1·0316	13·01	4·14	8·87	1·0317	12·93	4·06	8·87
December	1·0316	12·72	3·89	8·83	1·0315	12·88	4·05	8·83	1·0316	12·80	3·97	8·83
Average	1·0318	12·40	3·59	8·81	1·0316	12·64	3·84	8·80	1·0317	12·52	3·72	8·80
1915.												
January..	1·0318	12·64	3·80	8·84	1·0316	12·71	3·88	8·83	1·0317	12·68	3·84	8·84
February.	1·0316	12·50	3·72	8·78	1·0318	12·62	3·78	8·84	1·0317	12·56	3·75	8·81
March ..	1·0318	12·46	3·65	8·81	1·0317	12·56	3·75	8·81	1·0318	12·51	3·70	8·81
April ..	1·0318	12·36	3·54	8·82	1·0318	12·43	3·64	8·79	1·0318	12·40	3·59	8·81
May ..	1·0323	12·39	3·48	8·91	1·0319	12·62	3·75	8·87	1·0321	12·51	3·62	8·89
June ..	1·0322	12·25	3·36	8·89	1·0319	12·44	3·61	8·83	1·0321	12·35	3·49	8·86
July ..	1·0318	12·29	3·51	8·78	1·0313	12·56	3·81	8·75	1·0316	12·43	3·66	8·77
August ..	1·0317	12·46	3·67	8·79	1·0313	12·67	3·90	8·77	1·0315	12·57	3·79	8·78
September	1·0320	12·64	3·73	8·91	1·0319	12·93	4·01	8·92	1·0320	12·79	3·87	8·92
October ..	1·0321	12·72	3·78	8·94	1·0322	12·98	3·99	8·99	1·0322	12·85	3·89	8·96
November	1·0323	12·89	3·88	9·01	1·0322	13·05	4·04	9·01	1·0323	12·97	3·96	9·01
December	1·0319	12·80	3·88	8·92	1·0318	12·89	4·00	8·89	1·0319	12·85	3·94	8·91
Average	1·0319	12·53	3·67	8·86	1·0318	12·71	3·85	8·86	1·0319	12·62	3·76	8·86
1916.												
January..	1·0318	12·73	3·86	8·87	1·0317	12·79	3·92	8·87	1·0318	12·76	3·89	8·87
February.	1·0319	12·57	3·71	8·86	1·0319	12·69	3·82	8·87	1·0319	12·63	3·77	8·86
March ..	1·0320	12·50	3·65	8·85	1·0320	12·66	3·78	8·88	1·0320	12·58	3·72	8·86
April ..	1·0320	12·52	3·68	8·84	1·0317	12·65	3·83	8·82	1·0319	12·59	3·76	8·83
May ..	1·0321	12·42	3·54	8·88	1·0320	12·52	3·65	8·87	1·0320	12·47	3·60	8·87
June ..	1·0325	12·27	3·33	8·94	1·0321	12·65	3·74	8·91	1·0323	12·46	3·54	8·92
July ..	1·0316	12·35	3·56	8·79	1·0316	12·53	3·77	8·76	1·0316	12·44	3·67	8·77
August ..	1·0314	12·40	3·70	8·70	1·0309	12·80	4·11	8·69	1·0311	12·60	3·91	8·69
September	1·0316	12·56	3·76	8·80	1·0313	12·98	4·16	8·82	1·0315	12·77	3·96	8·81
October ..	1·0321	12·52	3·64	8·88	1·0317	12·92	4·07	8·85	1·0319	12·72	3·86	8·86
November	1·0323	13·00	3·97	9·03	1·0319	13·18	4·22	8·96	1·0321	13·09	4·10	8·99
December	1·0318	12·95	4·05	8·90	1·0318	13·05	4·15	8·90	1·0318	13·00	4·10	8·90
Average	1·0319	12·55	3·70	8·85	1·0317	12·79	3·94	8·85	1·0318	12·67	3·82	8·85

The general averages are confirmed by figures obtained from smaller series of 13,023, 12,646, and 8,704 samples.

The average percentages of fat for the years 1914, 1915, and 1916 (3·72, 3·76, and 3·82 respectively) show a progressive increase on the figure for 1913 (3·67), the average for 1915 being the highest on record since 1903, and that for 1916 being nearly equal to the 1903 percentage. Regarding the difference between the average fat percentages in the morning and evening milks, this was remarked by one of us to be less than usual (0·31) in 1913. The corresponding difference for 1914 was 0·25, that for 1915, 0·18, and that for 1916, 0·24, showing a progressive tendency towards approximation, which is seen to be chiefly due to increases in the figures for the morning milks, the increases in the evening milks being only 0·01 per cent. for each year, 1914 and 1915.

In 1914 the minimum fat percentage occurred in May, and as appreciable numbers of samples falling below 3·0 per cent. were noted in the morning milks from February to August inclusive, Table II., which shows the percentage numbers of such samples, has been extended to include these months. In 1915 and 1916 the minimum occurred in June, as is more usual, and appreciable numbers of samples falling below 3·0 per cent. only occurred in the morning milks of April, May, June, and July.

TABLE II.

Month.	1914.				1915.			
	2·9 to 3·0	2·8 to 2·9	2·7 to 2·8	Below 2·7	2·9 to 3·0	2·8 to 2·9	2·7 to 2·8	Below 2·7
February ..	0·6	0·7	0·6	—	—	—	—	—
March	1·3	0·7	0·4	0·4	—	—	—	—
April	1·8	1·2	0·5	0·8	0·8	0·4	0·2	—
May . ..	5·0	4·3	1·9	1·2	0·9	0·4	0·1	—
June	3·9	1·9	1·2	1·1	2·5	0·8	0·3	—
July	1·5	0·9	0·1	0·2	1·2	0·7	0·1	0·3
August . ..	1·3	0·5	0·3	—	—	—	—	—

In the three years the highest percentage of fat occurred in November, that observed in November, 1914 (4·06), and November and December, 1916, being exceptionally high. In the latter respect, as also in respect of the distribution of low fat percentages, the results of 1914 are comparable with those of 1912.

The usual fall in percentages of solids not fat was noticed in July and August of each year, but no very low percentages were recorded. In September the solids not fat were normal.

With a view of throwing some light on the decreasing difference between the morning and afternoon percentages of fat, and also for examining the variation in the fat, the number of samples giving results lying between each 0·1 per cent. of fat were tabulated for each month, the morning and afternoon results being kept separate; it was found that the 1914 results appeared to fall into regular series, but in 1915 there were such irregularities, almost certainly due to a larger personal equation of the assistants who had replaced those who had undertaken other duties, that the 1915 results were but little employed for critical examination; it was not thought worth while under these circumstances to tabulate the 1916 figures. The irregularities, which consisted in an abnormal grouping around certain percentages, would probably but little affect the averages, but would render the computation of the probable variation uncertain, and consequently they have only been used as broadly corroborating the conclusions deduced from the 1914 results; even the 1914 figures indicate that there is a tendency to obtain too many results at 3·0 and 4·0 per cent.

For each month in 1914 and 1915 the probable error was calculated by the usual formula $p=0{\cdot}6745\left(\frac{\Sigma(v^2)}{n-1}\right)$. If the results are arranged symmetrically around the mean, as is usually the case if the distribution is fortuitous, the sum of the squares of the deviations above the mean is very nearly equal to that of the squares below, and the curve obtained by plotting the numbers against the percentages is the probability curve; but if there is some disturbing influence, the sums of the squares above and below are unequal, and a skew curve results. This is most readily shown by doubling the sum of the squares above and below and calculating a plus and minus "probable error" from the doubled results. These are given in Table III.

TABLE III.

	1914.						1915.					
	Morning Deviation.			Afternoon Deviation.			Morning Deviation.			Afternoon Deviation.		
		−	+		−	+		−	+		−	+
January..	0·230	0·213	0·248	0·231	0·228	0·235	0·181	0·181	0·181	0·172	0·171	0·174
February.	0·218	0·206	0·229	0·245	0·250	0·240	0·154	0·150	0·157	0·175	0·170	0·179
March ..	0·216	0·207	0·225	0·247	0·247	0·248	0·183	0·175	0·190	0·189	0·175	0·202
April ..	0·205	0·212	0·198	0·238	0·238	0·238	0·182	0·170	0·193	0·226	0·219	0·234
May ..	0·181	0·174	0·187	0·217	0·220	0·213	0·195	0·175	0·214	0·216	0·211	0·221
June ..	0·193	0·191	0·194	0·205	0·207	0·203	0·195	0·172	0·219	0·230	0·222	0·235
July ..	0·173	0·164	0·182	0·221	0·221	0·221	0·231	0·214	0·246	0·243	0·253	0·232
August ..	0·205	0·189	0·220	0·223	0·226	0·219	0·241	0·239	0·243	0·266	0·274	0·258
September	0·178	0·167	0·189	0·222	0·224	0·220	0·222	0·215	0·229	0·250	0·253	0·248
October ..	0·198	0·179	0·214	0·223	0·218	0·229	0·231	0·223	0·239	0·236	0·245	0·227
November	0·220	0·221	0·219	0·201	0·199	0·203	0·260	0·256	0·264	0·265	0·279	0·250
December	0·213	0·211	0·214	0·186	0·187	0·185	0·259	0·247	0·271	0·264	0·271	0·258
Average	0·202	0·194	0·210	0·222	0·222	0·221	0·211	0·202	0·220	0·228	0·229	0·227

It is seen that while the afternoon figures give plus and minus "probable errors" which are nearly equal throughout, in almost every case throughout the twenty four months the plus probable error of the morning results is distinctly greater than the minus, and the results when plotted give very distinct skew curves.

It was decided, for the reasons given, to confine a further examination to the 1914 results, and as it was realised that the individual months were too much affected by " personal equation," it was decided to average them and confine the examination to the average.

In a paper by one of us (ANALYST, 1904, **29**, 180) it was shown that the results over a number of years agreed well with those calculated by the theory of probabilities, provided they were split up into two series, which were assumed to represent morning and afternoon results respectively. The average and the probable error were calculated in the usual way from the morning and afternoon results, and it was found that the afternoon results agreed very well with those calculated, but that the morning results showed very considerable divergences. The morning and afternoon results were added together, and were found to agree fairly well with those calculated by a combined formula, though the mean figures showed a much better agreement with a mean of the formulæ used to calculate the morning and afternoon results separately: better, indeed, than we expected to find, and this appeared to give a clue to the divergence of the morning results—*i.e.*, that the afternoon results contained some from morning milk (or milk of similar quality), and that the morning results contained many from afternoon milk; this was, indeed, known to be probable in some instances, as sometimes the morning and afternoon milks arrived together at the dairies and could not always be distinguished. By deducting from the proportion of samples falling between each percentage interval in the morning series one-third of the corresponding afternoon figures, and multiplying by $\frac{3}{2}$ a fresh series was obtained with plus and minus probable errors practically identical, and giving an average of 3·45 and a probable error of ±0·182; and by combining these figures with the afternoon figures in the proportion of 2 to 1, a fair agreement of the morning figures was obtained. (See Table IV., p. 123.)

It is a point for remark that the figure 3·45 is almost exactly 0·4 per cent. below the afternoon fat, as has been observed for so many years, and that the probable errors ±0·182 and ±0·253 obtained for the morning and afternoon milks respectively agree remarkably with those calculated formerly.

We have observed that the number of farms on which the percentage of fat in the morning milk is the same or very close to the afternoon milk has increased, and we conclude that the smaller difference between the morning and afternoon fat now observed is due to the morning milk now containing an increased proportion of richer milk than formerly, either (to a small extent) by the transposition of the milks, or by the morning milk being richer, owing to some cause, such as alteration in the times of milking, which we cannot definitely state.

TABLE IV.

	MEAN.			AFTERNOON.		MORNING.	
x	p			p		p	
	Found.	Calculated.		Found.	Calculated.	Found.	Calculated.
		a	b				
Below 2·7	0·002	0·002	0·0005	0·001	—	0·004	0·001
2·7	0·003	0·003	0·002	0·002	0·001	0·004	0·003
2·8	0·006	0·006	0·004	0·003	0·002	0·009	0·006
2·9	0·008	0·013	0·008	0·003	0·004	0·013	0·012
3·0	0·023	0·019	0·0175	0·012	0·008	0·034	0·027
3·1	0·031	0·030	0·031	0·015	0·014	0·048	0·048
3·2	0·048	0·044	0·0475	0·024	0·023	0·072	0·072
3·3	0·064	0·060	0·0655	0·037	0·035	0·090	0·096
3·4	0·084	0·077	0·0815	0·053	0·050	0·115	0·113
3·5	0·094	0·087	0·093	0·066	0·067	0·122	0·119
3·6	0·095	0·092	0·098	0·082	0·084	0·108	0·112
3·7	0·098	0·098	0·097	0·099	0·097	0·098	0·097
3·8	0·085	0·092	0·0915	0·100	0·105	0·069	0·078
3·9	0·080	0·087	0·0825	0·104	0·105	0·055	0·060
4·0	0·080	0·081	0·0715	0·111	0·099	0·049	0·044
4·1	0·063	0·064	0·060	0·086	0·086	0·040	0·034
4·2	0·048	0·050	0·048	0·070	0·070	0·026	0·026
4·3	0·035	0·036	0·0365	0·052	0·054	0·018	0·019
4·4	0·021	0·025	0·026	0·032	0·038	0·009	0·014
4·5	0·014	0·016	0·0165	0·021	0·025	0·007	0·008
4·6	0·008	0·009	0·010	0·012	0·015	0·004	0·005
Above 4·6	0·010	0·011	0·012	0·015	0·018	0·006	0·006

x = per cent. fat.

p = proportion of samples falling between the percentage of fat named and the one next above.

Formulæ used for—

Mean (a) $$p=\frac{1}{2\sqrt{\pi}}\left\{\int_{\frac{3\cdot57-(x+0\cdot1)}{0\cdot250}}^{\frac{3\cdot57-x}{0\cdot250}} e^{-\left(\frac{x}{0\cdot250}\right)^2} d\left(\frac{x}{0\cdot250}\right)+\int_{\frac{3\cdot84-(x+0\cdot1)}{0\cdot253}}^{\frac{3\cdot84-x}{0\cdot253}} e^{-\left(\frac{x}{0\cdot253}\right)^2} d\left(\frac{x}{0\cdot253}\right)\right\}$$

Mean (b) $$p=\frac{1}{3\sqrt{\pi}}\left\{\int_{\frac{3\cdot45-(x+0\cdot1)}{0\cdot182}}^{\frac{3\cdot45-x}{0\cdot182}} e^{-\left(\frac{x}{0\cdot182}\right)^2} d\left(\frac{x}{0\cdot182}\right)+2\int_{\frac{3\cdot84-(x+0\cdot1)}{0\cdot253}}^{\frac{3\cdot84-x}{0\cdot253}} e \left(\frac{x}{0\cdot253}\right)^2 d\left(\frac{x}{0\cdot253}\right)\right\}$$

Afternoon $$p=\frac{1}{\sqrt{\pi}}\int_{\frac{3\cdot84-(x+0\cdot1)}{0\cdot253}}^{\frac{3\cdot84-x}{0\cdot253}} e^{-\left(\frac{x}{0\cdot253}\right)^2} d\left(\frac{x}{0\cdot253}\right)$$

Morning $$p=\frac{1}{3\sqrt{\pi}}\left\{2\int_{\frac{3\cdot45-(x+0\cdot1)}{0\cdot182}}^{\frac{3\cdot45-x}{0\cdot182}} e^{-\left(\frac{x}{0\cdot182}\right)^2} d\left(\frac{x}{0\cdot182}\right)+\int_{\frac{3\cdot84-(x+0\cdot1)}{0\cdot253}}^{\frac{3\cdot84-x}{0\cdot253}} e^{-\left(\frac{x}{0\cdot253}\right)^2} d\left(\frac{x}{0\cdot253}\right)\right\}$$

NOTE BY H. DROOP RICHMOND.

In the recent appeal case of Hunt *v.* Richardson it was held by three Judges that no offence against the Sale of Food and Drugs Acts was committed by the sale of milk which was proved to be in the same state as yielded by the cows, even if far below the Board of Agriculture limits; while two other Judges were of the opinion that the case should be remitted to the justices to find whether the milk, although in the same state as yielded by the cows, was of merchantable quality. This decision has been made use of to a considerable extent in the defence of prosecutions, especially for the abstraction of cream; in my opinion, however, too much stress has been laid on the necessity of proving that the milk has not been tampered with, and far too little on proving that the natural separation of cream from milk on standing has not been counteracted. To take an example, if a sample of milk contained 2·5 per cent. of fat, the chance deduced from the results given above would be about 1,000 to 1 against its being genuine in the months of May or June, and far greater in other months; while the chances of its having attained that composition from the natural rising of cream not being counteracted by mixing would be something like 1,000 to 1 on. It is quite evident that to prove that the milk was sold in the same state as yielded by the cow, very definite evidence must be forthcoming of careful and complete admixture of the milk every time that a portion is withdrawn from a bulk after standing any appreciable time. As a rule there is much evidence as to non-tampering, and but little as to admixture, and the defence is really very weak. Another weakness of the defence is that frequently colouring matter is added, and this, though it may not appreciably affect the composition, prevents the proof that the milk was sold in the same state as yielded by the cows.

DISCUSSION.

Mr. C. H. **CRIBB** asked whether the composition of milk was likely to be affected by any changes in conditions due to the adoption of "summer time."

Mr. C. **REVIS** agreed with what the authors had said as to the importance of mixing. He believed that the occurrence of low percentages of fat was largely due to want of attention to this. When the milk from one farm was divided and sent to different destinations, it was possible that a churn here and there might be low in fat owing to imperfect mixing, but the occurrence of such samples through natural causes, even in such bad times as those of the past year, was rare, and he thought that the plea that the milk was as it came from the cow should not be accepted unless the whole of the churns sent out could be sampled and the true average composition of the milk ascertained.

Mr. **RICHMOND** said that before "summer time" was introduced he had feared that the alteration of milking-times might have a bad effect on the composition of the milk, but from a study of the figures subsequently obtained he could not see that anything of the kind had occurred.

* * * * *

STUDIES IN STEAM DISTILLATION— PART IV.: PROPIONIC, BUTYRIC, VALERIC, AND CAPROIC ACIDS.

By H. DROOP RICHMOND, F.I.C.

(*Read at the Meeting, March* 7, 1917.)

THE sample of propionic acid worked with was obtained from Kahlbaum; as a preliminary, 1·5 c.c. were diluted to 100 c.c. and 10 c.c. of this distilled. This was diluted to 100 c.c., and called fraction " A "; a further 70 c.c. were distilled and rejected, and the remaining 20 c.c. were washed out of the flask, made up to 100 c.c., and called fraction " B."

A and B were each distilled in fractions of 10 c.c. as previously described (ANALYST 1908, **33**, 305), with results as below.

Note.—The tables in this paper are condensed, and only give x, y, and a.

$$x = 1 - \frac{\text{water distilled per cent.}}{100} \qquad y = 1 - \frac{\text{acid distilled per cent.}}{100}$$

$$a = \frac{\log. y}{\log. x}.$$

First 10 c.c.			Last 20 c.c.		
x	y	a	x	y	a
0·8985	0·873	1·269	0·8995	0·8795	1·214
0·7985	0·7495	1·282	0·800	0·764	1·216
0·6985	0·636	1·263	0·700	0·6525	1·198
0·5985	0·522	1·268	0·600	0·541	1·204
0·498	0·415	1·258	0·4995	0·4365	1·196
0·3975	0·316	1·249	0·3985	0·3355	1·189
0·2965	0·222	1·239	0·2975	0·2405	1·177
0·198	0·1345	1·240	0·1975	0·149	1·174
0·096	0·058	1·215	0·096	0·068	1·149

As the mean factor for A was 1·256 and B 1·193, it was evident that the acid was not pure, and it was estimated to contain about 2 per cent. of acetic acid and 2·6 per cent. of butyric acid. The whole of the acid was fractionated; in the first two fractionations the portion boiling between 139·7° C. and 141·7° C. was collected; in the third that boiling between 140·2° C. and 141·2° C.; and in the fourth and fifth the portion boiling between 140·5° C. and 140·9° C. was taken, but little being removed below the lower temperature, and no higher fraction than 140·9° C. being collected in the fifth fraction; 1·5 c.c. of this was diluted to 100 c.c. and distilled as in the previous experiment, with results as follows:

First 10 c.c.			Last 20 c.c.		
x	y	a	x	y	a
0·900	0·8775	1·24	0·900	0·875	1·25
0·800	0·757	1·25	0·800	0·759	1·24
0·700	0·6425	1·24	0·700	0·642	1·24
0·600	0·530	1·24	0·600	0·534	1·23
0·500	0·425	1·23	0·500	0·425	1·23
0·400	0·324	1·23	0·400	0·3255	1·22
0·300	0·2295	1·22	0·300	0·230	1·22
0·200	0·1395	1·22	0·200	0·1415	1·22
0·100	0·063	1·20	0·100	0·061	1·22

It is seen that the two series of results are practically identical, and do not indicate any appreciable amount of impurity. As before, in calculating the ratio the first fraction has been neglected, and the other results were weighted from a consideration of the effect of 0·1 per cent. error in the percentage combined with a 0·05 per cent. error in the volume considered as a cumulative error; for propionic acid the relative weights of the fractions are:

Fraction ..	2	3	4	5	6	7	8	9
Weight ..	2	5	6	6	6	5	4	2

Seven other series from N/5 to N/100 were distilled, and the results need not be given in full, as they were of the same nature as those just given.

The factor deducted from the experiments is expressed by the formula 1·224 + 0·0222 log. 100 S. and the table below gives the results found and those calculated:

	FACTOR.	
S.	Found.	Calculated.
0·0084	1·221	1·222
0·0165	1·234	1·229
0·0213	1·225	1·231
0·033	1·238	1·236
0·083	1·243	1·244
0·166	1·252	1·251

A mixture of acetic and propionic acids was made containing 0·488 molecules of propionic to 0·512 of acetic acid, and the mean results indicated 0·493 molecules of propionic acid.

x	y	Calc. for Acetic.	Calc. for Propionic.	y Calc.	Ratio $\frac{P}{A+P}$.
0·900	0·9025	0·931	0·8755	0·904	0·513
0·7985	0·807	0·8585	0·7565	0·809	0·505
0·698	0·7115	0·782	0·641	0·714	0·500
0·5985	0·619	0·7045	0·5295	0·620	0·488
0·4985	0·523	0·6215	0·4215	0·5245	0·492
0·3985	0·429	0·533	0·320	0·430	0·488
0·2995	0·2375	0·333	0·1365	0·238	0·486
0·0995	0·132	0·206	0·0575	0·134	0·498

Considerable difficulty was experienced in obtaining butyric acid in a state of purity. Kahlbaum's acid was found to be of only approximate purity, as the following results show:

x	y	a
0·950	0·898	2·10
0·899	0·8085	2·00
0·800	0·747	1·955
0·700	0·5045	1·92
0·5985	0·373	1·925
0·499	0·268	1·895
0·3995	0·1795	1·875
0·2995	0·1085	1·84
0·1995	0·056	1·79
0·0975	0·0235	1·61

And another specimen which I had fractionated from a commercial butyric acid was used. After about ten fractionations, the portions boiling from 160·5° C. to 161·5° C. being collected in each case, comparatively small fractions being rejected at each fractionation, an acid was prepared, which gave the following results on distillation:

x	y	a
0·902	0·8045	—
0·803	0·644	2·00
0·704	0·4955	1·96
0·591	0·3525	2·05
0·497	0·252	2·07
0·406	0·1705	1·95
0·308	0·1025	1·90
0·209	0·050	1·89
0·105	0·011	1·98

Weighted mean = 1·99.

As this was not considered satisfactory owing to the continued fall in the factor, this was dissolved in water, and one-third distilled. Of the distillate a further third was distilled, and of this, again, one-third, and this distillate was distilled in fractions.

x	y	a
0·902	0·800	—
0·802	0·634	2·06
0·701	0·482	2·00
0·600	0·354	2·00
0·5005	0·246	2·01
0·400	0·1595	2·06
0·300	0·090	1·99
0·200	0·0415	1·99
0·098	0·012	1·89

Weighted mean = 2·01

The weights for butyric acid for fractions 2 to 9 are—

0·7	1·0	1·0	0·9	0·7	0·5	0·3	0·1

This indicated that an acid approaching purity was being obtained, and a considerable quantity of the acid was again distilled thus, and the first fractions converted into barium salts which were crystallised from alcohol.

Several series of results were obtained, all similar to that given above and leading to a mean factor of 2·00 for butyric acid; and it was noticed that the first fraction always led to a higher ratio, and a series distilled in an unjacketed flask with ample condensation gave a factor of 2·12.

x	y	a
0·900	0·798	2·14
0·799	0·618	2·14
0·699	0·462	2·16
0·597	0·332	2·14
0·497	0·231	2·10
0·395	0·142	2·10
0·295	0·078	2·09
0·199	0·032	2·13
0·094	0·009	1·99

Kahlbaum's iso-valeric acid was fractionated, and the fraction for 175°-176° C. collected; this was refractionated, and two fractions 175°-175·7° C. and 175·7°-176° C. collected. These polarised respectively −6·9° and −7·0° in a 200 mm. tube, and it was evident that further fractionation would not affect any appreciable separation of the iso- and active acids.

As valeric acid is not miscible with water in all proportions, the solubility at 100° C. was determined on the first fraction by shaking 1 c.c. with 8 c.c. of water in a test-tube immersed in boiling water for fifteen minutes and allowing the undissolved acid to separate; 1·5184 grms. of the solution contained 0·1362 grm. of valeric acid estimated by titration with N/10 alkali = 9·0 per cent.; the vapour pressure is given by Kahlbaum as 49 mm. at 100°, and these data allow of the calculation of the rate of volatility thus:

$$a = \frac{49}{760} \times \frac{91}{9} \times \frac{102}{18} = 3{\cdot}70$$

a figure which should agree approximately with that deduced for dilute solutions, but probably not agree exactly.

One c.c. of each fraction was made up to 100 c.c., and 5 c.c. distilled from each, then a further 40 c.c., which was rejected, and the remaining 50 c.c. collected. The four fractions were then distilled in fractions of 10 c.c. each, with results as below:

A.

Fraction 175°-175·7° C. First 5 c.c.

x	y	a
0·901	0·6795	—
0·801	0·4475	3·55
0·7005	0·2805	3·52
0·600	0·1625	3·52
0·500	0·086	3·52
0·399	0·0415	3·44
0·298	0·015	3·44
0·200	0·003	3·60
0·098	—	—

B.

Fraction 175°-175·7° C. Last 50 c.c.

x	y	a
0·9005	0·688	—
0·7995	0·456	3·38
0·6995	0·287	3·43
0·598	0·168	3·40
0·498	0·093	3·36
0·398	0·0455	3·32
0·2995	0·017	3·35
0·199	0·0065	3·08
0·098	0·001	2·94

C.

Fraction 175·7°-176° C. First 5 c.c.

x	y	a
0·900	0·6785	—
0·800	0·448	3·55
0·700	0·280	3·53
0·600	0·1595	3·58
0·500	0·0855	3·52
0·400	0·0405	3·48
0·300	0·016	3·41
0·1995	0·0035	3·50
0·099	—	—

D.

Fraction 175·7°-176° C. Last 50 c.c.

x	y	a
0·900	0·6845	3·49
0·800	0·454	3·37
0·7005	0·2945	3·38
0·6005	0·1745	3·36
0·4995	0·0945	3·22
0·3995	0·050	3·10
0·2995	0·022	3·10
0·1995	0·0065	—
0·0995	—	—

It is seen that there is no appreciable difference between the two fractions boiling at 175°-175·7° C. and 175·7°-176° C., but there was evidence of a small amount of acid being present which was less volatile in the last 50 c.c.; the mean values of a deduced from the first 5 c.c. (which represented 17 per cent. of the total acid) were 3·51 and 3·515 for the two fractions, and for the last 50 c.c. (representing about 9 per cent.) were 3·37 and 3·35. The latter values diminished gradually as the distillation proceeded, and it appeared from the results of the distillation that there was a small amount of an acid of considerably less volatility, which was reduced to an infinitesimal amount in the first 5 c.c. fractions; it appeared probable that the two valeric acids did not greatly differ in volatility.

Twenty-five c.c. of the fraction boiling at 175·7°-176° C. were dissolved in 600 c.c. of water and sufficient soda solution to give a solution neutral to phenolphthaleïn, and 28·5 grms. silver nitrate dissolved in 400 c.c. of water added, both solutions being hot, and cooled over-night. The precipitate was filtered over the pump and three times recrystallised from water, and a yield of 12·7 grms. of silver salts = 6·3 grms. of valeric acid (= 25 per cent.) was obtained. Four c.c. of nitric acid were added, and the valeric acid separated; this polarised $-0.37°$ in a 200 mm. tube.

One grm. + 3 c.c. N/10 strontia solution was made up to 100 c.c., and 5·2, 5·2-40 c.c., and 40-90 c.c. distilled; these three fractions were distilled in portions of 10 c.c. each.

A.

First 5·2 c.c.

x	y	a
0·9005	0·6865	—
0·801	0·454	3·53
0·7015	0·289	3·46
0·6005	0·166	3·50
0·499	0·0905	3·43
0·400	0·044	3·39
0·299	0·0165	3·38
0·1995	0·0045	3·34
0·0995	—	—

B.

5·2 c.c.-40 c.c.

x	y	a
0·899	0·682	—
0·800	0·453	3·50
0·700	0·286	3·47
0·6005	0·166	3·50
0·5005	0·089	3·47
0·401	0·415	3·47
0·301	0·0155	3·46
0·201	0·0035	3·52
0·0995	—	—

C.

Last 40-90 c.c.

x	y	a
0·900	0·684	3·48
0·800	0·454	3·47
0·700	0·286	3·46
0·600	0·168	3·44
0·499	0·090	3·39
0·399	0·0435	3·30
0·299	0·018	3·24
0·198	0·005	—
0·098	—	—

Finally, the mother liquors, which would contain a large proportion of active acid, were, after adding a quantity of nitric acid nearly sufficient to liberate the valeric acid, distilled to half their volume, and a portion of the distillate distilled in fractions as below:

x	y	a
0·900	0·685	—
0·8015	0·457	3·495
0·7005	0·284	3·52
0·6005	0·163	3·55
0·500	0·089	3·48
0·400	0·041	3·48
0·299	0·017	3·36
0·199	0·004	3·40
0·0985	—	—

The weights for valeric acid for the 2nd to 8th fractions are—1·0, 1·0, 1·0, 0·7, 0·4, 0·2, 0·06.

It is seen that the last 40-90 fraction gives a very slight indication of some less volatile acid (? nitric), and that the others give a value of a of 3·49 for the iso- acid and 3·505 for the acid containing a large proportion of active acid; also there is no indication of a change with concentration.

The value 3·50 may be adopted for both iso- and active valeric acids or a mixture of the two without appreciable error. A solution distilled in a flask without a steam-jacket gave a value for a of 3·69.

x	y	a
0·901	0·676	—
0·801	0·438	3·72
0·702	0·268	3·72
0·602	0·153	3·70
0·501	0·079	3·65
0·401	0·035	3·66
0·301	0·014	3·52
0·201	0·005	—
0·101	0·002	—

Normal caproic acid from Kahlbaum was fractionally distilled; boiling commenced at 190° C., and a few drops of milky liquid passed over before 204° C., to which the temperature rapidly rose, and fractions from 204·5° to 205·5° C., and 205·5° to 206·5° C. were collected, there being a fairly large fraction up to 210° C.

The fraction 204·5° to 205·5° C. was refractionated, and the portion below 204·5° C. rejected (a slight milky drop coming over first); a fraction 204·5° to 205·5° C. was collected, and the fraction 205·5° to 206·5° C. then added, and a small amount more distilled at 204·5° to 205·5° C.; there was an appreciable fraction above 205·5° C., and this was slightly dark. The middle fraction was refractionated, and the portion 204·5° to 205·5° C. collected; it was judged that the lower boiling fraction (quite small) contained traces of water, and that there was no serious amount of substance boiling below 204·5° C., but there appeared to be an appreciable fraction above 205·5° C., which did not appear to diminish in the last fraction.

One c.c. of this fraction was shaken with 500 c.c. of water, and all dissolved, and 150 c.c. of this were distilled in fractions. The value of a fell steadily from 3·6 to 1·7, and it was evident that there was some acid present which was less volatile.

To remove this, 50 c.c. were distilled from another 100 c.c., made up to 100 c.c., and distilled in fractions, giving a fairly concordant set of values for *a* rather over 3·5, but falling away to 3·0 at the end.

It was thought from the results of the fractionation and the distillation of the solution that there might be a formation of lactones; 0·2215 grm. took 18·85 c.c. N/10 alkali for direct titration, and 19·24 c.c. after boiling with excess of alkali and titrating back. The first result indicates a molecular weight of 117·3, and the latter of 115·0; and as it was probable that the acid contained a little water, it appears that the sample was nearly pure caproic acid, mixed with its lactone. A quantity of N/10 sulphuric acid slightly in excess of the alkali was added, and 50 per cent. was distilled, made up to 100 c.c., and distilled in fractions.

x	*y*	*a*
0·950	0·827	3·70
0·851	0·546	3·75
0·751	0·340	3·77
0·651	0·2045	3·70
0·550	0·110	3·69
0·450	0·055	3·64
0·248	0·007	3·56

Another portion of the acid was boiled with excess of soda, an equivalent amount of sulphuric acid added, the volume made up to 100 c.c., and fractions of 11 c.c., 15 c.c., and 50 c.c. distilled; each of these, which contained approximately one-third of the acid, were made up to 100 c.c. and distilled in fractions, giving mean results for *a* of 3·71, 3·73, 3·70, agreeing within the limits of experimental error.

From the results of several distillations the mean value of *a* of 3·71 was deduced, a value that was much lower than expected.

Diethyl acetic acid, for which I am indebted to Mr. J. Marshall, and which was made in the Sir Jesse Boot's Research Laboratories, was prepared by heating di-ethyl-malonic acid to 190° C.

The following table gives the results of the distillation:

x	*y*	*a*
0·902	0·629	—
0·8035	0·362	4·75
0·7035	0·194	4·76
0·6005	0·093	4·70
0·4995	0·041	4·65
0·3975	0·015	4·76
0·2975	0·003	4·78
0·195	0·001	—
0·100	—	—

The mean figure (4.75) was confirmed by another experiment.

Taking the results for 0·01 N solution, the factors agree fairly well with those calculated by the formula:

$$a = 0{\cdot}4013 \times 1{\cdot}72 ,$$

where *n* is the value in the formula $C_nH_{2n+1}COOH$.

	a	n	$0{\cdot}4013 \times 1{\cdot}72^n$
Formic	0·4013	0	0·4013
Acetic	0·677	1	0·69
Propionic	1·224	2	1·18
Butyric	2·00	3	2·04
Valeric	3·50	4	3·51

The results for the caproic acids do not agree with the formula, and a study of the results obtained with the other isomers will form the subject of a later communication.

D. C. Dyer (*J. Biol. Chem.*, 1917, **28**, 445, see p. 149) has lately published a steam distillation method in which the volume is kept constant at 150 c.c., and under these circumstances, as pointed out by me (ANALYST, 1908, **33**, 209), the curve is a simple logarithmic one; the results give a straight line if plotted out on a logarithmic chart for a single acid, but a curved one for a mixture, and the probable natures and proportions of the acids may be approximately read from the curves and tables given.

Boekhout and de Vries (*Centr. Bakt. Par.*, 1916, **11**, 46, 505) have lately studied Duclaux's method, and find that if the differences between each fraction be calculated as percentages of the acid present at the commencement of the distillation, and these expressed as a ratio of the amount distilled to 110 c.c. (the original volume adopted by Duclaux), constant figures are obtained for each fraction, being—

Formic acid	3·5
Acetic acid	5·9
Propionic acid	11·8
Butyric acid	19·1
Valeric acid	26·0

These figures, if multiplied by 0·11, should give the same values as I have found for *a*, and, indeed, show an approximate agreement. This mode of calculation is only a crude method of differentiation, and better results are obtained by the method that I have used.

The bulk of this work was done in the laboratories of the Aylesbury Dairy Company, and it was completed in the laboratories of Messrs. Boots' Pure Drug Co., Ltd., to both of whom I wish to express my thanks, and I have to acknowledge the assistance of Messrs. W. B. Walker and S. Darnell.

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STUDIES IN STEAM DISTILLATION—PART V.: SOME APPLICATIONS OF DUCLAUX'S METHOD.

BY H. DROOP RICHMOND, F.I.C.

(*Read at the Meeting, March* 7, 1917.)

THE use of Duclaux's method is best exemplified by the analysis of compounds which contain or yield acids of the acetic series. In many cases, where there is a simple mixture of two acids, there is no difficulty in the application of the method, the amount of acid distilled being calculated for each of the acids present, and the ratio of them deduced by a simple proportion sum for each fraction; a satisfactory agreement between the ratios thus deduced will show that no other acids are present, and the mean ratio will give the molecular proportions.

In certain cases, however, the analysis is not so simple, and some of these may be usefully discussed.

ACETIC ANHYDRIDE.

This substance has been taken as an instance, not only because a slight modification of Duclaux's method is advisable, but because there appears to be a considerable divergence of opinion as to the common impurities and the methods of analysis. Quite recently C. E. Sage (*Perfumery and Essential Oil Record*, December, 1916, p. 388), after pointing out that a direct titration, calculating all the acidity as derived from acetic anhydride, gives erroneous results, advocates the calculation of the composition on the assumption that acetic acid and acetic anhydride and no other substance are present. Considering that acetic anhydride has as its raw material commercial acetates which are known to contain other homologues, it is not surprising that commercial acetic anhydride should contain similar impurities, chiefly butyric acid, and Sage's method of calculation will give errors as great as those he seeks to avoid.

For the estimation of the anhydride there is an excellent method due to Menschutkin and Wasiljew (*J. Russ. Chem. Soc.*, 21, 190), which has been largely overlooked, possibly owing to its having appeared in Russian, and not having been abstracted in the English journals nor appearing in textbooks except that of Treadwell (1915 edition, p. 585), who condemns it, in my opinion on the insufficient ground that, owing to the rise of temperature, the acetic acid combines with the aniline as well as the anhydride; this is prevented by the ice-cooling.

Edwards and Orton (ANALYST, 1911, **36**, 417) use 2·4·dichloroaniline.

It will be useful to give the method used in the laboratory of Messrs. Boots' Pure Drug Co., Ltd.

Acetic Anhydride Estimation.

(Per cent. Acetic Anhydride; per cent. Acetic Acid; per cent. Butyric Acid.)

1. *Direct Titration.*—Weigh 25 c.c. N/1 NaOH in a 50 c.c. stoppered flask. Add 1 c.c. (approx.) of the anhydride and weigh again. Difference=wt. taken

Shake to dissolve, and titrate with N/2 HCl and phenolphthaleïn. Calculate c.c. N/1 NaOH required for 1 grm.

2. *Aniline Titration.*—Weigh 10 c.c. aniline in a 100 c.c. flask. Cool in ice and add 1 c.c. (approx.) of anhydride, keeping in ice during the addition, and weigh again. Difference=weight taken. Add 50 c.c. water, and titrate with N/1 NaOH and phenolphthaleïn. Calculate c.c. N/1 NaOH required for 1 grm.

Then (c.c. in 1 − c.c. in 2) × 10·2 = per cent. of anhydride as acetic.

Now (2 × c.c. in 2 − c.c. in 1) = “n” c.c. due to $H\bar{A}$ and $H\bar{B}$, and $H\bar{A}$ and $H\bar{B}$ per grm.

$$= \frac{100 - \text{per cent. of } (CH_3CO)_2O}{100} = x \text{ grm.}$$

and

$$\text{If all acetic acid} = \frac{x}{0{\cdot}06} = \text{“ a ” c.c.}$$

$$\text{If all butyric acid} = \frac{x}{0{\cdot}088} = \text{“ b ” c.c.,}$$

(“ a ” c.c. − “ n ” c.c.) = proportion due to butyric acid = *B*.

(“ n ” c.c. − “ b ” c.c.) = proportion due to acetic acid = *A*.

Per cent. acetic acid—

$$= \frac{A}{A+B} \times (100 - \text{per cent. anhydride}).$$

Per cent. butyric acid—

$$= \frac{B}{A+B} \times (100 - \text{per cent. anhydride}).$$

Butyric Acid.—One c.c. is weighed into a small flask containing 10 c.c. water + 15 c.c. N soda, and allowed to stand for one hour, and washed into a distillation flask with about 5 c.c. water. About 25 c.c. are distilled, 12 c.c. CO_2 free water are added, and distilled, repeating six times. The distillates are received in a 100 c.c. flask and made up to volume. Residue in distillation flask should be just alkaline to phenolphthaleïn. The distillation flask is washed out and drained and the distillate added, draining the flask, and distilled, collecting distillate in fractions of 10 c.c. in stoppered cylinders. (Note volume of each accurately.)

Titrate each separately with N/5 baryta, and after nine fractions have been collected, wash out condenser, add washings to residue in flask, and titrate.

Total acidity = sum of 9 fractions + residue. (Calculated as c.c. N/1.)

Express the acidity of each fraction as percentage of total acidity. Calculate the amount that would be distilled if the acid were acetic and butyric, respectively, by the formulæ—

$$y = x^{0.686} \text{ and } y = x^2$$

$$y = \frac{\text{per cent. acid left in flask}}{100}$$

$$x = \text{volume left in flask}$$

and subtract per cent. calculated for acetic from that found for each fraction, and divide by difference between per cent. calculated for acetic and butyric.

Average values for 2nd to 7th fractions (which should not differ greatly): then per cent. butyric acid

$$=\frac{\text{Total acidity} \times \text{average} \times 0{\cdot}088 \times 100}{\text{weight taken}}.$$

A typical experiment will illustrate—

Mean value of direct titration = 19·26 c.c. N/1 per grm.
Mean value of aniline titration = 9·96 c.c. N/1 per grm.

Calculated composition:

Acetic anhydride	94·9 per cent.
Acetic acid	1·5 ,,
Butyric acid	3·6 ,,
Direct titration calculated as acetic anhydride ..	98·2 ,,
Direct titration calculated on the assumption that only acetic acid and acetic anhydride are present	88 ,,

x	y	Corr. for First Fraction.		Calc. Acetic.	Calc. Butyric.	Ratio $\frac{B}{B+A}$.
		x	y			
0·8985	0·927	—	—	—	—	—
0·8015	0·851	0·892	0·918	0·925	0·796	0·054
0·7025	0·772	0·781	0·832	0·844	0·626	0·055
0·604	0·6935	0·675	0·748	0·764	0·456	0·052
0·5065	0·6085	0·563	0·656	0·674	0·317	0·050
0·407	0·519	0·453	0·560	0·581	0·205	0·056
0·307	0·423	0·342	0·456	0·479	0·117	0·064
0·206	0·3165	0·229	0·340	0·355	0·079	0·054
0·103	0·189	0·115	0·203	0·227	0·013	—

As the calculation of the ratio has been made after rejecting the first fraction, it must be remembered that about 20 per cent. of the butyric acid and only 7 per cent. of the acetic have been removed, and consequently the ratio must be calculated thus:

$$\text{Butyric}=\frac{0{\cdot}055}{0{\cdot}8}=0{\cdot}0069$$

$$\text{Acetic}\ =\frac{0{\cdot}945}{0{\cdot}93}=1{\cdot}025$$

$$\therefore \text{ the ratio of butyric}=\frac{0{\cdot}069}{1{\cdot}025+0{\cdot}069}=0{\cdot}063.$$

As 1·0637 grms. were weighed out and the total acid distilled took 5·27 c.c. N/1 alkali, the percentage of butyric acid in the acetic anhydride is—

$$\frac{5{\cdot}27 \times 0{\cdot}063 \times 0{\cdot}088 \times 100}{1{\cdot}0637} = 2{\cdot}7 \text{ per cent.}$$

0·31 c.c. for butyric acid per grm. = 2·7 ,,
0·35 c.c. for acetic acid per grm. = 2·1 ,,

Adding up with 94·9 per cent. acetic anhydride to 99·7 per cent.

I am inclined to attach more importance to the determination of butyric acid by Duclaux's method than to that calculated from the two titrations, because the latter is subject to a combined error of titration, and also because a very small percentage of other substance would make a considerable error. The method of neutralising 75 per cent. of the acid may give slightly low results, as the acid combined with the soda will be in proportion to the amounts of each acid present, and inversely as the strength of the acid; but, as butyric is removed so much faster than acetic, the amount remaining at the end of the distillation must be very small.

It is quite evident that in the presence of even small amounts of butyric acid the mode of calculation advocated by Sage may lead to far greater errors than those which he tries to avoid.

This method does not distinguish between butyric acid existing as the acid itself and that present as anhydride, but an examination of the acid obtained by the hydrolysis of the acetanilide formed would indicate what proportion is present as butyric anhydride.

I have to acknowledge the assistance of Mr. D. A. Langsdale in this part of the work.

Acetyl Chloride.—This is examined in the same way as acetic anhydride; such minute traces of hydrochloric acid distil over that there is no need to remove them before distilling in fractions.

No samples of acetyl chloride have contained butyric acid, but it is conceivable that it may be present.

The analysis of this presents no difficulty, a total acidity estimation, a determination of chlorine, and a phosphorus estimation, usually by a differential titration to phenolphthaleïn and methyl orange of the residue left on evaporating an aqueous solution with bromine, and moistening two or three times to get rid of all volatile acid, being usually sufficient data. The phosphorus calculated to $POCl_3$, the rest of the chlorine to acetyl chloride, and the remainder of the acidity to acetic anhydride usually add up very close to 100 per cent.

The density affords a check on the $POCl_3$ determinations, as this compound has a density of 1·7 and acetyl chloride of 1·106.

Purity of Acetyl Compounds.—Duclaux's method may be used to establish the purity of acetyl compounds by separating the acetic acid by hydrolysis, and distilling it in fractions; thus, acetyl salicylic acid has been examined, and it has been found that the volatile acid distils as acetic, the fractions agreeing almost exactly with those calculated for acetic. It is necessary to remove all the salicylic acid by extraction with ether, as otherwise its slight volatility will interfere very considerably.

I am indebted to Mr. A. D. Powell for an experiment which shows that salicylic acid has a value for a of 0·107.

x	y	a
0·902	0·992	—
0·802	0·979	0·111
0·697	0·964	0·111
0·599	0·949	0·107
0·499	0·931	0·106
0·403	0·909	0·107
0·303	0·881	0·109
0·200	0·814	0·107
0·100	0·786	0·105

As the solubility of salicylic acid in water at 100 is 1 in 9, this value of a corresponds to a vapour pressure of about 1·2 mm.

It may be useful to point out that when testing for small quantities of salicylic acid in the presence of acetic acid it is necessary to neutralise exactly, and the above figures show that it is of considerable advantage to distil 90 per cent. of the solution, as, while nearly 80 per cent. of the acetic acid is thus removed, only 15 per cent. of the salicylic acid is lost, and the delicacy of the test is thus greatly enhanced.

Substituted Malonic Acids.—The starting-points of many synthetic compounds are the substituted malonic acids, and Duclaux's method affords a means of testing their purity; thus, the ethylation product of malonic acid may give a product consisting of malonic, ethyl-malonic, and diethyl-malonic acids, and these are readily converted into the corresponding members of the acetic series by heating to 190°, when a quantitative conversion with evolution of CO_2 takes place, and the resulting product may be examined by Duclaux's method.

x	y	Distilled Calc. for 8 per cent. Acetic.	y Recalculated after deducting 8 per cent. Acetic.	Calc. for Butyric.	Calc. for Diethyl Acetic.	Ratio $\frac{\text{B}}{\text{B}+\text{D.-E.-A.}}$
0·899	0·739	0·006	0·723	0·809	0·606	0·42
0·799	0·544	0·011	0·516	0·640	0·341	0·41
0·701	0·398	0·018	0·365	0·490	0·183	0·41
0·604	0·289	0·023	0·251	0·365	0·091	0·42
0·500	0·198	0·030	0·160	0·250	0·037	0·42
0·398	0·134	0·038	0·099	0·159	0·013	0·41
0·2955	0·084	0·045	0·052	0·088	0·003	0·42
0·194	0·049	0·054	0·025	0·038	0·000	—
0·092	0·020	0·064	0·006	0·010	—	—
1·000	0·000	0·080	—	—	—	—

Mean ratio .. { 0·415 molecules of butyric.
0·585 molecules of diethyl acetic.

Or calculated composition—

Acetic	8 molecules.
Butyric	38 ,,
Diethyl acetic	54 ,,

The analysis of a sample of the mixed esters of these acids, for which I have to acknowledge the help of Mr. C. Seaton, will illustrate the method of deducing the composition for the results.

The ester was hydrolysed with an excess of N/1 soda, the resulting solution evaporated to remove alcohol, and made up to 100 c.c. with the addition of about 0·1 c.c. more N/1 sulphuric acid than was equivalent to the soda added. Fractions of 10 c.c. were distilled, and after 90 c.c. had been distilled continued additions of 10 c.c. of water were made, and distilled off till all the acid had been obtained.

The calculations of the proportions of the various acids may be made in two ways—either by calculating the values of y for each of the acids, making each set of values into simultaneous equations, and calculating the percentages by the method of least squares, or by inspection of the values at the two ends of the distillation. The former method suffers from the defect that, while the method of least squares requires that all the observations have equal value, it is known that the weight to be attached to each fraction varies widely with the value of a, and therefore the less scientific method of inspection gives results at least as reliable.

Consideration of the figures calculated for each acid shows that in the 9th fraction the amount of diethyl acetic acid is infinitesimal, and that therefore that value is wholly due to acetic and butyric; and a consideration of the first fraction, in which the amount of acetic acid is small, indicates that the amount of butyric acid must be somewhere in the nature of 40 per cent. It is therefore obvious that the percentage of acetic acid must be very close to 8 per cent., and the amount of acetic acid in each fraction has been calculated on this assumption and deducted from the total, and the resulting figures recalculated so as to make the total of the butyric and diethyl acetic acids equal to 1. By simple proportion sums the ratio of butyric acid in each fraction has been calculated with a very satisfactory agreement, and from this the composition of the mixture deduced as—

Acetic ester	5·5	per cent.
Butyric ester	34·5	,,
Diethyl acetic ester	61·0	,,

This investigation was carried out in the analytical laboratory of Messrs. Boots' Pure Drug Co., Ltd., to whom my thanks are due.

DISCUSSION.

Mr. T. H. DURRANS asked if Mr. Richmond had estimated sulphur as well as phosphorus impurities in acetic anhydride. The sulphur impurities might be of the sulphur chloride or of the thio-acetic anhydride type. He also asked whether Mr. Richmond had any figures showing the depression of the boiling-point of acetic anhydride in the presence of acetic acid, when the distillation was conducted without fractional condensation.

Mr. G. N. HUNTLY suggested that possibly pure propionic acid could be more readily prepared synthetically than by repeated fractionations of the commercial product. Such impurities as might occur in the synthetic product would not be likely to consist to the same extent of isomers as when the commercial product was fractionated. For substances boiling below 150° he had found that the Young evaporator column far surpassed all others in efficiency and speed.

Mr. J. A. PICKARD said that, having had occasion during the past year or two to examine considerable quantities of acetic anhydride, chiefly from the point of view of strength, he had gone pretty thoroughly into the methods of analysis available, and he agreed with Mr. Richmond that much still remained to be desired. He had finally adopted the method, alluded to by Mr. Richmond, of neutralising with alkali and titrating back with standard acid. The degree of accuracy attainable by this method, however, was not much greater than 1 per cent. of actual anhydride in the sample, and it, of course, involved the assumption that nothing was present except acetic anhydride and acetic acid. He thought that that assumption was justified, for of all the samples he had examined—Swiss, Dutch, American, and, latterly, English—he had only found one which gave any positive indication of butyric acid—*i.e.*, which yielded a product smelling of butyric acid. He should rather doubt whether commercial acetic anhydride at present did contain any considerable quantity of butyric anhydride. The percentage of acetic anhydride was, as a rule, about 88, and the remainder appeared to be acetic acid.

Dr. COLMAN remarked that he understood Mr. Richmond, when speaking of "fractional distillation," to confine himself to fractional distillation proper—*i.e.*, where the vapours evolved were all condensed without any alteration of their composition by previous fractional condensation. The term "fractional distillation" was so often used as including fractional condensation as well—though the two were, of course, totally distinct—that he wished to make quite certain that Mr. Richmond was speaking of fractional distillation only.

Mr. RICHMOND said that he used the term "fractional distillation" in the sense indicated by the Chairman—*i.e.*, as excluding fractional condensation. In a previous paper he had described an apparatus in which such condensation was eliminated as far as possible by means of a steam-jacket. The quantity of sulphur in the samples of acetic anhydride which he had examined had been found to be very small—very much less than the phosphorus.

The apparatus which he chiefly used for distillation was the rod-and-disc still-head. It was not, perhaps, the most efficient, but it was convenient and cheap; and when, as in some of these cases, the quantities fractionated were quite small, it was, he thought, a more practicable form than the evaporator still-head. His experience, unlike that of Mr. Pickard, was that acetic anhydride frequently contained butyric acid, and even as little as 2 or 3 per cent. gave rise to a considerable difference between the results arrived at by titration and by the method of Menschutkin and Wasiljew. In some cases of which he had records the percentage was as high as 17 or 18, and from some of the samples he had actually separated the butyric acid. Possibly, however, his experience might not be comparable with that of Mr. Pickard, for, while he always made a special point of looking for butyric acid, he did not gather that Mr. Pickard went much beyond the evidence of smell.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Note on Ghee. K. C. Browning and M. Parthasarathy. (*J. Soc. Chem. Ind.*, 1917, **36,** 118.)—Bolton and Revis have stated (ANALYST, 1910, **35,** 343; 1911, **36,** 392) that the Reichert-Meissl value of ghee usually approaches or even exceeds 30. Kesava Menon (*J. Soc. Chem. Ind.*, 1910, **29,** 1428) records 26 for cow ghee and 18 for buffalo ghee of undoubted genuineness. K. H. Vakil (ANALYST, 1915, **40,** 284) also found values between 24 and 25. The authors, having also found much lower values than Bolton and Revis in many ghees they had reason to believe genuine, prepared several samples in the laboratory from milk they had seen drawn from the cow or buffalo. Four buffalo ghees gave Reichert-Meissl values of 18·9, 18·9, 27·0, and 30·2; five cow ghees, 21·4, 22·3, 23·9, 28·0, and 20·9. Ghees prepared in their laboratory in Ceylon from imported frozen Australian butter had Reichert-Meissl values 29·4 and 28·0. G. C. J.

NOTE.—There appear to have been several attempts recently to show that pure ghee may have very low Reichert-Meissl values. This may be true in the case of samples made in the laboratory from the milk of single animals, but this in no way proves that such values are to be considered normal, just as has been the case with similar values for butterfat. To admit the validity of such values as a guide to the possible results obtained from commercial samples is to leave a very extensive loophole to wholesale adulteration. The figures given by Bolton and Revis have been confirmed by Trimen (ANALYST, 1913, **38,** 246).—EDITOR.

Estimation of Free Alkali Hydroxide in Soap. V. A. Izmailski. (*J. Russ. Phys.-Chem. Soc.*, 1916, **48,** 411-432; through *J. Soc. Chem. Ind.*, 1917, **36,** 295.)—For the estimation of the free alkali hydroxide in soap neither the alcohol method nor the barium chloride method yields results which are accurate or reproducible by different workers. The errors of the alcohol method are due principally to the capability of colloidal soap in an alcoholic medium of adsorbing free alkali, and the difficult solubility in alcohol of the "alkali soap" thus formed and its marked retention of the filtrate. When barium chloride is used, special precautions are necessary to prevent hydrolysis of the soap itself. From the results of experiments made by the author the following method has been devised: A portion of the soap is freshly cut from the interior, and about 100 grms. weighed into a flask of about 400 c.c. capacity fitted with a rubber stopper, and dissolved in 200 c.c. of boiling distilled water. To the hot solution is gradually added 20 c.c. of neutralised (towards phenolphthaleïn) barium chloride solution containing 30 grms. of the salt to 100 grms. of water, the liquid being rotated and boiled for a short time until the precipitate no longer settles down. During the dissolution and boiling, the flask is loosely closed with the stopper. When the precipitate settles the flask is cooled under the tap and tightly stoppered, the cold liquid being immediately filtered through a rapid filter into a conical flask and the filter washed with cold boiled water. Any precipitate remaining in the original flask is washed with three portions of boiled and cooled water, amounting to 100 c.c., in the closed flask. The liquid is titrated with N/10 acid in presence of phenolphthaleïn. The values thus obtained, which the author terms the "alkali numbers," are characteristic for different types of soap.

Detergent Action of Soap. S. U. Pickering. (*J. Chem. Soc.,* 1916, **111,** 86-101.) — Although the detergent action of soap is much increased by the presence of excess of alkali, it exists to some extent independently of such excess (ANALYST, 1916, **41,** 311, 352). It is in part due to its power of emulsifying oil, the globules of which become enclosed in a pellicle which prevents them rendering contiguous substances oily; in part to the lowness of surface tension between oil and soap solution (*cf*. Hillyer, *J. Amer. Chem. Soc.,* 1903, **25,** 511). The union of dirt with the acid soap produced by hydrolysis is also a factor, but a more important one still is the fact, often overlooked, that oils, even paraffin oils, dissolve in soap to form soluble compounds which may contain in some cases nearly equal weights of oil and soap. Thus, when a potassium soap and paraffin oil are mixed together (this taking some little time for complete incorporation), the mixture suddenly becomes opaque and almost solid, and " wets " the containing vessel. In the case of a soda soap the final mixture is almost transparent. The mixtures are permanent if a concentrated soap is used, and when treated with excess of water they dissolve completely, forming solutions which are either clear—except for the presence of some acid soap—or, if the proportion of oil is larger, milky, owing to the presence of an emulsion which separates as a cream on the surface in the course of some hours or days. Except when the oil added is small in amount, a certain proportion of it becomes emulsified and incapable of combining with the soap owing to the protecting pellicle; hence considerable excess of oil must be taken for the soap to combine with the maximum amount of oil possible. The compound formed is not decomposed by excess of water, but dilution of the soap previous to its treatment with oil results in much less oil combining with it, because a larger proportion of the latter becomes emulsified. The combination of soap with oil is accompanied by a series of physical changes explicable by the nature of the products formed—a soluble limpid compound on the one hand, and an emulsion which is almost solid on the other. The proportions of oil and soap which will unite depend on the chemical and not merely physical nature of the reagents, and an appreciable heat disturbance, either negative or positive, accompanies the reaction. Naphthalene does not behave towards soap as paraffin does, but dissolves in it to a limited extent, some of the crystalline substance separating on cooling or dilution. The presence of naphthalene decreases the amount of paraffin dissolved by soap. Some remarks on the value of soap-paraffin and soap-naphthalene mixtures as insecticides are included by the author (*cf. J. S.E. Agric. Coll.,* 1896, **5,** 51). H. F. E. H.

Spinacene: a New Hydrocarbon from Certain Fish-Liver Oils. A. C. Chapman. (*J. Chem. Soc.,* 1917, **111,** 56-69.) — A sample stated to consist of cod-liver oil was found by the author to have the following constants: Specific gravity (15°/15°), 0·8666; saponification value, 22·5; iodine value (Wijs), 358; unsaponifiable matter, 89·1 per cent.; iodine value of unsaponifiable matter, 376·2; free fatty acid (as oleic), 0·42 per cent.; bromine precipitate insoluble in ether, 76·5 per cent. From these it was concluded that 89 per cent. of some unsaturated hydrocarbon oil was present, raising doubts as to the oil being a liver oil at all. Further inquiries showed that the oil was undoubtedly obtained from the livers of two fishes known in Portugal as "Barroso" (*Centrophorus granulosus*) and "Carocho" (*Scymnus lichia*), both belonging to the *Spinacidæ* or *Squalidæ* family of the shark group. Upon fractionally distilling the residual oil after the removal of the saponifiable portion, a small amount of cholesterol was found to separate from the first fraction, while the great bulk of the oil proved to be a hydrocarbon which on distillation over sodium yielded a colourless and fairly mobile oil with a faint odour suggesting lemon oil terpenes, and burning with a smoky flame; the boiling-point was 280° C. (corr.)/17 mm.

The average of five analyses showed carbon 87·75 per cent. and hydrogen 12·45 per cent.; $C_{30}H_{50}$ requires carbon 87·8 and hydrogen 12·2 per cent. A freezing-point determination in benzene pointed to 375 as the molecular weight; $C_{30}H_{50}$ requires 410. The oil is optically inactive and does not solidify at $-20°$ C.; the specific gravity at 15°/15° C. is 0·8641; and the index of refraction at 20° gave the following values:

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

At 15° C. the index of refraction for the D line is 1·4987, and the specific refraction calculated by the formula $\frac{n^2-1}{(n^2+2)d}$ is 0·3394, the molecular refraction being 139·1. Taking Conrady's average numbers for the atomic specific refractions (D line), $C_{30}H_{50}$ with six ethenoid linkings requires 137·7.

The viscosity as determined by time of flow through the aperture of a Redwood viscometer showed a time of flow of 78 seconds for 50 c.c. as compared with 370 seconds for rape oil. On prolonged exposure to an atmosphere of oxygen, 1·662 grms. of spinacene absorbed 0·397 grm. of oxygen and became very viscous. Thin films form a hard skin on exposure to air similar to linseed oil. A number of halogen and nitrogen derivatives were prepared (*cf.* also *J. Ind. and Eng. Chem.*, 1916, **8,** 889).

H. F. E. H.

Volatile Reducing Substance in Cider Vinegar. R. W. Balcom. (*J. Amer. Chem. Soc.*, 1917, **39,** 309.)—The volatile reducing substance obtained by the distillation of vinegar was first observed by Farnsteiner, who showed that it was neither furfural nor formaldehyde. It reduces Fehling's solution readily even in the cold, and separates silver from alkaline silver solutions. Pastureau (*J. Amer. Chem. Soc.*, 1903, **25,** 29-31) identified acetylmethylcarbinol in the distillates from some abnormal vinegars, and prepared from it a crystalline osazone melting at 243° C. He gave reasons for disbelieving that diacetyl was present. The author confirms Pastureau's conclusions, but has found diacetylmethylcarbinol in all the normal samples of cider vinegar examined. An average value for this substance expressed in terms of invert sugar is about 0·25 to 0·30 grm. per 100 c.c. Estimations of the nitrogen in the diacetylphenylosazone prepared from the distillate showed 21·08 and 21·01 per cent. of nitrogen; theory requires 21·05 for this derivative. Acetylmethylcarbinol may be considered as a normal constituent of cider vinegar (*cf.* ANALYST, 1913, **38,** 565).

H. F. E. H.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Physiological and Chemical Valuation of Adrenaline Solutions. J. S. White. (*Pharm. J.*, 1917, **98**, 159-160.)—Adrenaline solutions are very liable to undergo oxidation, with consequent loss of activity; the oxidation is accompanied by the development of a pink colour which changes to red and then to brown, and a brown precipitate forms. The solution is suitable for use, although weak, even when it has a red colour, but when the brown coloration appears the solution should be rejected. The only satisfactory means of determining the strength of an adrenaline solution is the physiological method depending on the transitory rise in blood-pressure produced by the intravenous injection of the solution, as compared with the rise in pressure produced by a standard adrenaline solution. The following chemical method may, however, be used to ascertain the approximate strength of such solutions; it depends on the pink coloration which is obtained when adrenaline is heated with potassium iodate and hydrochloric acid. Five c.c. of the adrenaline solution are mixed with 5 c.c. of dilute hydrochloric acid (2·5 c.c. N/10 hydrochloric acid in 100 c.c. of water) and 5 c.c. of 0·2 per cent. potassium iodate solution; the mixture is heated nearly to boiling, and the colour observed after fifteen minutes. The standard is prepared by similarly treating 5 c.c. of pure adrenaline solution containing 1 part of the substance in 50,000 parts of water. To test the commercial powdered gland, 0·01 grm. of the sample is treated with the above-mentioned quantities of hydrochloric acid and potassium iodate solution. It may be mentioned that adrenaline solutions have been sold containing sulphurous acid, which, whilst in no way retarding oxidation, prevents the change in colour, so that a casual observation affords no evidence of the value of the solution. W. P. S.

Colouring Matter of Red Torulæ. A. C. Chapman. (*Biochem. J.*, 1916, **10**, 548.)—Growths on agar of red torulæ were dried and ground with sand, followed by extraction with chloroform and carbon bisulphide, both of which solvents gave deep red solutions, leaving on evaporation a coloured residue containing fat and some phytosterol. The chloroform solution on exposure to light quickly faded, suggesting that the colouring matter resembled carrotene, and in addition it was insoluble in water, and dissolved in concentrated sulphuric acid with a deep blue colour. A comparative examination of the absorption spectra of pure carrotene obtained from carrots and the red torula colouring matters revealed important differences, and it must be concluded that the torulæ either contain some substance in addition to carrotene, or that the colouring matter is a different substance altogether (ANALYST, 1912, **37**, 199, 596). H. F. E. H.

Evidence of the Existence in Malt of an Enzyme Hydrolysing the Furfuroids of Barley. J. L. Baker and H. F. E. Hulton. (*J. Chem. Soc.*, 1917, **111** and **112**, 121-130.)—Furfural was estimated throughout by the authors' modification (ANALYST, 1916, **41**, 244) of Flohil's method (*Chem. Weekblad*, 1910, **7**, 1057) as elaborated by Eynon and Lane (ANALYST, 1912, **37**, 41). The furfural and Fehling's solution were treated in a boiling-water bath for forty minutes under a reflux condenser, and the cuprous oxide obtained weighed as CuO. Experimental evidence was obtained by various methods that the insoluble furfuroid matter present in brewer's grains was capable of being made to yield a small proportion of soluble furfural-yielding substances with a reducing action on Fehling's solution (pentose sugars) when acted upon by the enzymes in air-dried green malt. It is also shown that excised barley embryos when grown on sand moistened with cane-sugar only increased in weight and furfuroid content, while there was transference of insoluble furfuroid matter from the barley endosperm to the embryo when the seeds were allowed to germinate in the ordinary manner, involving the enzymic hydrolysis of the endosperm furfuroids. Pentosans have not previously been shown to be amenable to the action of a "pentosase." H. F. E. H.

Pectic Substances of Plants. S. B. Schryver and D. Haynes. (*Biochem. J.*, 1916, **10,** 539-547.)—The materials extracted comprised turnips, strawberries, apples, and rhubarb stems, the first named giving the most satisfactory yield. Plant juices, with the exception of that of the apple, contain but little pectinogen, and the great bulk is obtained by a process of extraction with warm 0·5 per cent. ammonium oxalate from the residue remaining after the expression of the juices, followed by concentration of the extract to small bulk and precipitation with acidified alcohol (95 per cent.). The gelatinous precipitate so obtained is washed with alcohol and finally air-dried, when it is obtained as a granular white powder. The yield from 100 kilos of turnips is 355 grms., which loses about 25 per cent. in the steam-oven. The pectinogen so obtained is a single substance of acidic character, and is somewhat slowly soluble in water, yielding viscous, slightly opalescent solutions which are distinctly acid to phenolphthaleïn. A solution of pectinogen made neutral to phenolphthaleïn by caustic alkalis yields no precipitate on the addition of either dilute acid or a dilute solution of a calcium salt, but if kept in alkaline solution for a short time readily undergoes conversion into another substance, also of acidic character, called "pectin," soluble in alkalis and precipitated from its alkaline solutions by acids as a gel insoluble in water. It differs from pectinogen in being insoluble in water, and by the fact that the solution of its sodium salt gives a gelatinous precipitate with sodium chloride. A solution of pectinogen also gives a gel when allowed to stand at room temperature with an excess of calcium hydroxide solution. Pectins from the different fruits and vegetables above mentioned have been prepared, and their elementary analyses agree well with the formula $C_{17}H_{24}O_{16}$. On distillation with hydrochloric acid, pectinogen yields furfural in such quantity as to indicate that one pentose group is present in each complex of seventeen carbon atoms. Pectin would not appear to be a carbohydrate, but an acid. H. F. E. H.

Starch in Bracken Fern. A. E. Shipley. (*Times*, March 15, 1917.)—The author quotes figures of J. E. Purvis in which the starch content of the rhizomes of *Pteris aquilina* is given as varying from 1·7 to 2·3 per cent. As a commercial source of starch this does not compare favourably with the potato, but the raw material costs nothing and exists in enormous quantities. The starch content of the rhizomes is highest in the spring, but the starch itself is not of a good quality, and is a light slaty-grey in colour.

H. F. E. H.

ORGANIC ANALYSIS.

Interpretation of Coal Analysis. E. G. Bailey. (Ann. Meeting, International Railway Fuel Assoc.; through *J. Inst. Brewing,* 1917, **23,** 133-138.)—The usual analysis of coal gives the percentage of moisture, volatile matter, fixed carbon, ash, and sulphur, in addition to the calorific value. The calorific value is perhaps the most important factor, but if the others are not taken into account erroneous conclusions may be drawn. The non-combustible matters present have such a modifying influence that not infrequently the better of two coals, judged only by their calorific values, proves the worse in practice. The author discusses the influence of various factors, determined by analysis, on the actual stoking value of coal.

The real basic impurities in coal, from the point of view of generation of heat, are oxygen, nitrogen, and ash. Sulphur is generally classed as an impurity because its heating value is so low that it does not compensate for the detrimental qualities of this constituent. In the accompanying table the amounts of the constituent elements present in the volatile matter are shown. The percentage of volatile matter in a coal is not a measure of the value of the coal, for much depends on the nature of the volatile matter and how much of it is combustible. Moreover, in the combustible matter itself the proportion of available hydrogen to carbon affects the heating value.

Analysis of a Typical West Virginia Coal.

Constituents per Cent. of Coal.					B.T.U., per Pound.	Calculated B.T.U., per Pound of Coal.
Moisture	2·01	H	0·22	2·01 water	None	—
		O	1·79			
Volatile	37·31	H	4·86	5·38 water	None	—
		O	4·78	4·26 available H	62,000	2,641
		C	26·65		14,500	3,464
		N	0·23		None	—
		S	0·79		4,050	32
Fixed carbon	52·13	C	49·18		14,500	7,131
		N	1·20		None	—
		S	1·75		4,050	71
Ash	8·55				None	—
						13,339
B.T.U. by calorimeter						13,811

The percentage of moisture in coals varies widely according to their character. It is much higher in lignite and sub-bituminous coals than in bituminous or semi-bituminous kinds. Anthracite coal, on the other hand, has a slightly higher percentage of moisture than semi-bituminous coals. Many people have considered that the percentage of moisture was such a variable quantity, depending on weather conditions, etc., that true comparison could only be obtained on a dry basis, and they therefore reduce all analyses to this basis. This is likely to lead to very erroneous conclusions. For instance, if Illinois coal, which normally contains about 12 per cent. of moisture, is compared on a dry basis with bituminous coal from the Pittsburg or West Virginia district, which contains usually about 3 per cent. of moisture, the former will appear about 9 per cent. better than it should do. In order to get a uniform basis of comparison, it is right to compare different shipments of coal from the same region on a dry basis, but coals from different districts and of different characters should be compared on a basis which takes into account the normal moisture-contents fairly representative of the different districts.

A coal which normally has a high moisture-content usually has a relatively large proportion of its volatile matter in the form of combined water, and this water is as unproductive of heat as the ordinary moisture of the coal. The only practical means of allowing for the effect of this combined water is to determine the calorific value of the coal, for such coals have low calorific values per pound of matter other than moisture and ash.

The most important impurity in coal is the ash. It almost invariably contains alumina, silica, iron, lime, magnesia, titanium, alkalis, etc. The relative proportions of these constituents may vary widely in different coals, and their effect upon the behaviour of the coal is determined by such complex laws that it is practically impossible to use the analytical data as a trustworthy means of determining the character of the ash for comparative purposes. An ash which does not clinker gives little trouble, and is not much, if any, more detrimental than so much moisture. It is merely an inert substance that produces no heat. It does not seriously obstruct air-passages, and can easily be shaken through the grate. But an ash which melts into a clinker is more difficult to get rid of, and it may adhere firmly to the bars and obstruct the air so completely that the heat of the fuel-bed causes the bars to burn. Hitherto practically the only method of ascertaining how the ash of a coal would behave was by an actual trial; but such trials do not always afford trustworthy means of comparison, for some stokers make more clinkers than others from the same coal.

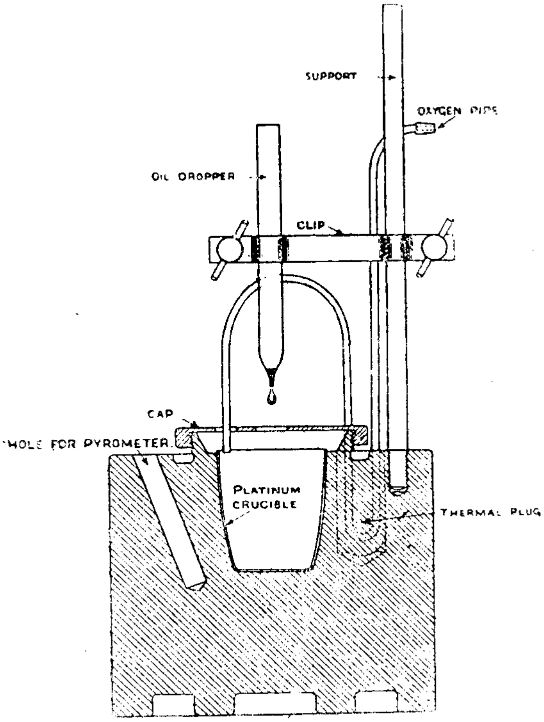
A study of this phase of the fuel problem some years ago led the author to conclude that everything depends on the temperature at which the ash fuses and the temperature to which it is actually subjected in practice. Some coal ash has such a high temperature of fusion that, there are practically no fuel-bed conditions which will produce troublesome clinker from it. Another ash with a slightly lower fusing temperature will form a porous, spongy clinker which does not seriously obstruct the flow of air and is not difficult to remove. An ash of still lower fusing temperature—*e.g.*, 2100° F.—will not only become melted under average conditions, but will be heated several hundred degrees above its melting-point, in which case it runs down and spreads out in a thin sheet over the grate bars.

When a coal is burned the ash is not entirely liberated until it reaches the lower part of the fuel-bed, where the incoming air maintains a lower temperature than obtains in the zone 4 to 6 inches above the grate. So it is often possible to get satisfactory results from a coal of which the ash fuses at 2300° F., although the temperature of the fuel bed may be 2500° F. Some clinker will, of course, be formed, but it is not of an extremely objectionable character if the firing is properly done; it accumulates gradually, and is more or less open and does not obstruct the air beyond the critical limit. But if another stoker should handle the same coal, differently slicing or working the fire and causing the ash, which has already been liberated from the coal in the lower and cooler part of the fuel-bed, to be thrown up again into the hotter zone, it will melt into a very fluid mass and spread out over the grates in a thin sheet, obstructing the air to a serious extent.

It is frequently considered that the percentage of sulphur is a true indication of the clinkering property of a coal. The estimation of sulphur in coal originated with the steel-works chemist, for in his case sulphur is extremely detrimental, but for steam coal it is of minor importance. It is true that in some coalfields the clinkering property of coal from different mines does vary to some extent with the sulphur-content, but the constituent which really affects the clinkering property is iron, and this usually increases or decreases with the sulphur. There are so many exceptions to the rule connecting with sulphur-content, or even the iron-content, with the clinkering property of coal, that dependence upon either is apt to lead to erroneous conclusions. One of the worst clinkering coals in the United States has a sulphur-content below 0·25 per cent.

Several of the largest stationary power plants in America make determinations of the fusing temperature of the ash, in addition to the regular analysis of each shipment of coal. This determination has not yet been standardised in the laboratory to the same extent as the determination of calorific value and other factors. In the author's opinion the method which will ultimately prove most suitable for this determination will be one that adheres most closely to practical conditions by reproducing, as far as possible, the conditions which obtain in the fuel-bed.

Colour Reactions of Aromatic Aldehydes. P. Pooth. (*Schweiz. Apoth. Zeit.*, 1916, **54**, 377-382; through *J. Chem. Soc.*, 1917, **112**, ii., 52.)—The condensation of aromatic aldehydes with sulphonated aromatic amino-compounds leads to the formation of characteristic, distinctly coloured azomethines, which can be employed in the identification of aldehydes. Aromatic aldehydes yield more distinct colorations with naphthionic than with sulphanilic acid; in most cases the azomethine separates directly on cooling. The test is performed as follows: 3 to 4 c.c. of an aqueous solution of sodium sulphanilate or naphthionate (10 per cent.) are heated in a porcelain dish on the boiling-water bath; a boiling alcoholic solution of the aldehyde is added, which causes the appearance of a pale yellow to red coloration, and the solution is evaporated to dryness, the colour generally being deepened thereby. Before evaporation, a few drops of the solution are removed, diluted with water, cooled, and treated with a few drops of dilute sulphuric acid; in many cases the colour is deepened, in others completely changed. Certain of the reaction products, particularly those derived from nitro-aldehydes, are sensitive to light. The products obtained from substituted aldehydes are less stable.



Spontaneous Ignition Temperatures of Liquid Fuels for Internal Combustion Engines. H. Moore. (*J. Soc. Chem. Ind.*, 1917, **36,** 109-112.)—The determination of this constant is important, both for engines which receive the fuel and air before the compression stroke (petrol engines) and for engines which compress the air alone and inject the fuel into the cylinder about the end of compression (Diesel engines). For use with the first type of engine, the constant should not be too low, or pre-ignition can only be avoided by the use of relatively low compression pressures and consequent loss of efficiency. Diesel engines, on the other hand, depend on spontaneous ignition of the charge, and this should take place at a reasonably low temperature, or the necessary pressures may be so high as to introduce mechanical difficulties.

Holm has described an apparatus (*Zeitsch. angew. Chem.*, 1913, 273) for determining spontaneous ignition temperatures, but the author found this insufficiently delicate for his researches with Diesel engines, and in consequence he designed the apparatus now described. It consists of a diffusion block of mild steel bar of 4 inches diameter, 3¼ inches deep, the base being turned as illustrated to afford greater heating surface. The upper end of the bar is machined to fit exactly the platinum crucible, which is 35 mm. in diameter at the top. A screwed-on cover protects the upper end of the crucible from draughts. The cover is provided with two holes, one for air inlet and one for oil inlet. The air is preheated to the temperature of the experiment, passing through a thin copper coil situated in a chamber inside the block. A thermometer and a thermo-couple pyrometer are fitted into the diffusion block as close as possible to the base of the crucible, and show the temperature of the experiment. Air is passed through the apparatus at the rate of three bubbles a second, a sulphuric acid wash-bottle enabling one to count the bubbles. When the temperature of the block is constant at a desired temperature one drop of the fuel under examination is allowed to fall through the hole in the centre of the cover of the instrument. If the temperature is higher than the ignition point an explosion occurs one second after the introduction of the oil. By repeating the experiment the lowest temperature at which ignition takes place is rapidly determined. The results obtained by different experimenters, using the same instrument, agree within 3° C. G. C. J.

Impure Picric Acid as a Source of Error in Creatine and Creatinine Estimations. O. Folin and E. A. Doisy. (*J. Biol. Chem.*, 1917, **28**, 349-356; through *J. Soc. Chem. Ind.*, 1917, **36**, 235.)—Attention is directed to the fact that certain specimens of picric acid, particularly those sold in the wet condition, contain some impurity, and, owing to the more or less intense coloration they give when neutralised with sodium hydroxide, are quite unsuitable for use in the colorimetric determination of creatinine. When 20 c.c. of saturated picric acid solution are treated with 1 c.c. of 10 per cent. sodium hydroxide solution, the coloration obtained and observed after fifteen minutes should be not more than about twice as deep as the colour of the saturated picric acid solution.

Method of Steam Distillation for the Determination of Volatile Fatty Acids, including a Series of Colorimetric Qualitative Reactions for their Identification. D. C. Dyer. (*J. Biol. Chem.*, 1917, **28**, 445-473; through *J. Soc. Chem. Ind.*, 1917, **36**, 236.)—In the steam distillation method described, the volume of the solution from which the acids are distilled is maintained constant at 150 c.c. throughout the distillation. Under these circumstances the distilling constants (proportions distilling over in succeeding fractions) are indicated by straight lines when plotted on a simple logarithmic chart, whilst the distilling variables of mixtures of these acids are indicated on the same chart by curved lines. With neighbouring acids the curves are very flat, and the further the acids comprising the mixture are removed from each other (in the series) the greater will be the curvature of the graph. The lowest acid of the series in a mixture may be identified with certainty, since the line representing the distilling constant will eventually reach a point where it will begin to run parallel to some straight line on the chart which represents that acid. This same point indicates where the other acid of the mixture has run out, and the probable nature of this second acid may be found by reference to a table which is given. The qualitative tests described for the identification of the volatile acids depend on the different solubilities of the iron and copper salts of the acids in amyl alcohol, ether, and petroleum spirit.

Duclaux's Method for the Estimation of Volatile Fatty Acids. F. W. J. Boekhout and J. J. O. de Vries. (*Centr. Bakt. Par.*, 1916, ii., **46**, 505-513; through *J. Chem. Soc.*, 1917, **112**, ii., 50.)—The authors have investigated Duclaux's method (*Ann. de l'Inst. Pasteur*, 1895), and confirm the figures given in his tables for formic, acetic, and propionic acids; in the case of butyric and valeric acids, the results obtained were somewhat different from those recorded by Duclaux. It is shown that if the differences between the quantities of acid found in each successive fraction of the distillate are calculated into percentages of the acid remaining in the flask at the commencement of the distillation of each fraction (this quantity of residual acid being first calculated into 110 c.c. of the solution), a constant number is obtained for each fraction, and is the same for each individual acid. This number is 3·5 for formic acid, 5·9 for acetic acid, 11·8 for propionic acid, 19·1 for butyric acid, and 26·0 for valeric acid. This method may be applied to the analysis of mixtures of the acids.

Gasometric Estimation of Amino-Nitrogen in Worts, Extracts, etc. R. Emslander. (*Zeitsch. ges. Brauw.*, 1916, **39,** 265-267; through *J. Inst. of Brewing*, 1917, **23,** 116.)—The method described, like that of van Slyke, is based on the measurement of the volume of nitrogen produced by the action of nitrous acid on the liquid under investigation, the reaction involved being represented by the equation—

$$R \cdot NH_2 + HNO_2 = R \cdot OH + H_2O + N_2.$$

The apparatus consists of a gas burette having alternative connections by a three-way cock at its upper end with a gas-evolution bottle on the one hand and a Hempel gas pipette containing a 2·5 per cent. solution of caustic soda saturated with potassium permanganate on the other. The burette itself is filled with a concentrated solution of ferrous sulphate, and is provided with a levelling vessel in the usual way. The gas-evolution bottle, 50 c.c. capacity, has a stopper fitted with (1) a capillary tube for connection with the burette, (2) a small tap-funnel containing octyl alcohol (to prevent frothing), (3) a large tap-funnel, and (4) a burette containing the liquid to be analysed. The bottle is first filled with 40 c.c. of sodium nitrite solution (3 parts of sodium nitrite to 10 parts of water) and 10 c.c. of glacial acetic acid. Oxides of nitrogen are evolved, and the stopper is at once fixed in the bottle, the cock of the large tap-funnel being left open so that the evolved gas forces the liquid up into this funnel. When the bottle is about half full of gas, communication is opened with the gas burette, and the nitrite mixture is allowed to flow from the tap-funnel into the bottle until the latter is again quite full. The displaced gas, thus transferred to the burette, is afterwards ejected from the latter by raising the level of the ferrous sulphate solution until the burette is again filled with liquid. In this way all air is swept out of the apparatus.

All connections except that between the bottle and the gas burette having been closed, the liquid to be analysed is run into the bottle from the burette containing it. If frothing occurs, a little octyl alcohol is also run in. The evolution of gas, assisted by frequent shaking, is allowed to proceed for five minutes, in which period all the nitrogen is evolved. The whole of the gas in the bottle is then driven over into the burette by running nitrite mixture into the bottle from the tap-funnel. The greater part of the oxides of nitrogen present in the gas mixture in the burette is absorbed by shaking with the ferrous sulphate solution. The residual gas is then driven over into the Hempel pipette and shaken vigorously with the alkaline permanganate solution, and the pure nitrogen remaining is again transferred to the burette and measured with the usual precautions; 1 c.c. of nitrogen (corrected or the tension of aqueous vapour) at 0° C. and 760 mm. pressure corresponds to 0·6253 mgrm. of amino-nitrogen.

Estimation of Total Nitrogen. E. Justin-Mueller. (*Bull. Sci. Pharmacol.*, 1916, **23,** 167-169; through *J. Chem. Soc.*, 1917, **112,** ii., 39-40.)—When organic substances are destroyed in the presence of mercury according to Kjeldahl's method, a portion of the ammonia remains combined in the form of mercury ammonium compounds, and is not estimated by the method of Ronchèse (ANALYST, 1907, **32,** 303). Low results are also obtained after addition of sodium sulphide or hypophosphite, but, according to the author, the results are accurate when potassium arsenite is used to decompose the mercury-ammonium compounds. The estimation is performed in the following manner : Urine (10 c.c.) is heated with concentrated sulphuric acid (5 c.c.) and mercury (about 0·1 grm.). If the urine contains sugar the quantity of acid is increased in the ratio of 10 per cent. of the sugar content. As soon as the solution becomes colourless the heating is discontinued, the solution cooled, and diluted to 50 c.c. with water. Five c.c. of the dilute solution are mixed with 10 c.c. of the arsenite solution and 5 drops of phenolphthaleïn, and neutralised by sodium hydroxide (10 per cent.); the precipitate is allowed to settle for a few seconds, filtered, the residue washed three times with water, and the ammonia estimated in the filtrate by the formaldehyde method of Ronchèse. The potassium arsenite solution is prepared by dissolving arsenious oxide (5 grms.) with the help of potassium hydroxide (11·20 grms.) or N/1 potassium hydroxide (200 c.c.), and making up the solution with water to 1,000 c.c.

Estimation of Total Sulphur in Leather. L. E. Levi and A. C. Orthmann. (*Chem. News,* 1917, **115,** 55-56.)—The sulphuric acid is precipitated as barium sulphate after the organic matter has been destroyed by boiling the leather with a mixture consisting of potassium dichromate 50 grms., water 150 c.c., and concentrated hydrochloric acid 50 c.c. One grm. of the fat-free leather is heated to boiling with 20 c.c. of the dichromate mixture, 10 c.c. of hydrochloric acid are then added, and the heating continued until all organic matter has been destroyed. The solution is now boiled for three minutes, 50 c.c. of water and 5 c.c. of alcohol are added, the mixture is boiled until the dichromate is reduced and the alcohol and aldehyde expelled, and the sulphate then precipitated by the addition of barium chloride solution. If the leather contains talc or other insoluble substance the solution must be filtered before the barium chloride is added. The results obtained by the method agree with those found by the bomb, the nitric acid, and the sodium carbonate methods.

W. P. S.

Identification of Phenols. E. E. Reid. (*J. Amer. Chem. Soc.,* 1917, **39,** 304.)—An improvement on the Schotten-Baumann reaction as a means for identifying the phenols is the formation of their *p*-nitrobenzyl ethers, which crystallise readily and have convenient melting-points; *p*-nitrobenzyl bromide reacts readily with salts of many acids to form esters, and this same reagent combines with the sodium or potassium phenolates to form the ether—

$$pNO_2C_6H_4CH_2Br + NaOC_6H_5 = pNO_2C_6H_4CH_2OC_6H_5 + NaBr.$$

The reaction is a very clean one, and a pure product is obtained directly; the chloride should work in most cases as well as the bromide.

Into a 100 c.c. flask are measured 25 c.c. of N/5 alkali in 95 per cent. alcohol, and to this is added a moderate excess of the phenol; usually this will be about 1 grm.

for phenols of molecular weight under 200. To this solution is added 1·0 grm. of *p*-nitrobenzyl bromide, and the whole is heated on the steam-bath under a reflux condenser for one hour, the progress of the reaction being shown by the precipitation of sodium or potassium bromide. About 5 or 10 c.c. of water are then added, which dissolves the bromide, and the solution is quickly cooled whilst vigorously shaken to cause the formation of small crystals.

The solution should be made just alkaline with caustic soda during the separation of the crystals, to prevent the separation of the excess of phenol, which might contaminate the *p*-nitrobenzy ether; this is filtered off, dissolved in boiling 95 per cent. alcohol, and again thrown out by the cautious addition of water. The following ethers have been made:

Phenyl *p*-nitrobenzyl ether [$C_6H_5OCH_2C_6H_4NO_2$], m.-pt. 91° C.
o-Cresyl *p*-nitrobenzyl ether [o-$CH_3C_6H_4OCH_2C_6H_4NO_2$], m.-pt. 89·7° C.
m-Cresyl *p*-nitrobenzyl ether [m-$CH_3C_6H_4OCH_2C_6H_4NO_2$], m.-pt. 51·0° C.
p-Cresyl *p*-nitrobenzyl ether [p-$CH_3C_6H_4OCH_2C_6H_4NO_2$], m.-pt. 88° C.
Thymyl *p*-nitrobenzyl ether [$CH_3(C_3H_7)C_6H_3OCH_2C_6H_4NO_2$], m.-pt. 85·5° C.
Eugenyl *p*-nitrobenzyl ether [$C_3H_5(OCH_3)C_6H_3OCH_2C_6H_4NO_2$], m.-pt. 53·6° C.
Vanillyl *p*-nitrobenzyl ether [$CH_3O(CHO)C_6H_3OCH_2C_6H_4NO_2$], m.-pt. 124·5° C.

H. F. E. H.

Analysis of Acetate of Lime. S. H. Collins. (*J. Soc. Chem. Ind.*, 1917, **36**, 68-70.)—This process is described in connection with a portable apparatus for the distillation of wood. Two grms. of the acetate are distilled with 15 c.c. of syrupy phosphoric acid in a large flask into which water is admitted from a Marriott dripping-bottle at the rate of about 4 drops per second. Both the distillation flask and the receiving flask are provided with soda-lime tubes to prevent any admission of carbon dioxide from the air. The liquid is distilled at such a speed that about 50 c.c. are always present in the distilling flask, and the distillate is received in 25 c.c. of N/1 sodium hydroxide solution, which is subsequently titrated with N/5 sulphuric acid, with phenolphthaleïn as indicator. In the case of pure acetates the whole of the acid distils in 300 c.c., but for very crude products, which contain a larger proportion of acids of higher boiling-point, it may be necessary to distil as much as 1,200 c.c. In any case it is advisable to continue the distillation until an extra 100 c.c. has been obtained, after all acid has apparently been driven over. An addition of 1 c.c. to the amount of sulphuric acid used in the titration is made as a correction for the alkali neutralised by the carbonic acid in the distilled water introduced into the flask.

C. A. M.

INORGANIC ANALYSIS.

Estimation of Manganese in High-Speed Steels. C. T. Nesbitt. (*Chem. News*, 1917, **115**, 61-62.)—The author was led to this research by the difficulty experienced in procuring bromine. Other oxidising agents were tried for precipitating manganese from the filtrate from a basic separation, but all the methods tried were abandoned, either because the results were insufficiently accurate or because the processes involved were too tedious. Failing bromine to complete an analysis begun with an acetate separation, the author can recommend only the following modification of the bismuthate process for the estimation of manganese in high-speed steels proper—that is to say, steels containing high percentages of tungsten and chromium, tungsten-chrome-vanadium, or tungsten-chrome-vanadium-molybdenum.

The drillings (1·1 grm.) are dissolved in 12 c.c. hydrochloric acid, 5 c.c. nitric acid are added, and the solution is evaporated to syrupy consistency. Sulphuric acid (7 c.c.) is added, and the sides of the beaker are washed down once with water. The beaker is kept at the edge of the hot plate for twenty minutes, heated more strongly until the contents give rise to fumes, evaporation being continued for fifteen minutes. This tends to reduce chromium, which is essential to success. The cooled residue is taken up in 30 c.c. of dilute (1 : 1) nitric acid and 20 c.c. water, the solution boiled and tungstic oxide filtered off on pulp. To the filtrate 15 c.c. concentrated nitric acid are added, the mixture is boiled, and a pinch of bismuthate added. After clearing with sulphurous acid and boiling until the excess is just removed (but not more than a minute longer or there is risk of chromium re-oxidising), the solution is rapidly cooled and 0·2 grm. sodium bismuthate added. The ordinary bismuthate process is then followed—that is to say, the solution is filtered through asbestos into excess of N/10 ferrous solution, washing with 3 per cent. nitric acid, and the excess of ferrous solution titrated with N/10 permanganate. One c.c. N/1 ferrous solution = 0·1 per cent. manganese. For success with high-speed steels tungsten must be thoroughly oxidised and removed, and chromium properly reduced by strong fuming with sulphuric acid and final treatment with sulphurous acid. The initial solution in hydrochloric acid actually saves time, although the hydrochloric acid has subsequently to be expelled, solutions made in sulphuric acid direct being very difficult to evaporate without loss. The method is accurate and twice as fast as any other reliable method.

G. C. J.

Estimation of Molybdenum by Potassium Iodate. G. S. Jamieson.

(*J. Amer. Chem. Soc.*, 1917, **39**, 246-249.)—The method depends on reduction of the molybdenum to Mo_2O_3 by means of amalgamated zinc, receiving the reduced solution (which is very susceptible to oxidation by air) in a hydrochloric acid solution of iodine monochloride, and estimation of the molybdenum by titration with potassium iodate. Unlike the permanganate titration, iodate carries the oxidation readily only as far as the stage Mo_2O_5, further oxidation proceeding so slowly (2 to 3 days) that it is not practicable to wait for it.

$$KIO_3 + Mo_2O_3 + 2HCl = Mo_2O_5 + ICl + KCl + H_2O.$$

A Jones reductor, at least 20 cm. in height, and preferably longer, is used; it is filled to within 3 cm. of the top with 30-mesh amalgamated zinc resting on a 2 cm. mat of glass wool on a platinum disc. Previously to making a reduction, a 500 c.c. titration bottle is charged with 5 c.c. of iodine monochloride solution, 25 c.c. of hydrochloric acid, 5 c.c. of water, and 7 c.c. of chloroform, and placed in a pan of cold water to cool the reduced solution rapidly. The reductor, set up in another bottle, is heated with dilute hydrochloric acid and 100 c.c. of hot water. When this has run out, the reductor is transferred to the bottle in cold water, and a measured amount of the molybdenum solution, acidified with 20 c.c. of dilute (1 : 1) hydrochloric acid, and heated to 50° C., is passed very slowly through the reductor. The flask is rinsed with dilute (1 : 2) hydrochloric acid several times, and the washings passed through the reductor and followed by a further 50 c.c. of dilute acid. The exposure of the zinc during the reduction causes no error, as would be the case with a permanganate titration, because hydrogen peroxide does not react with iodine monochloride or potassium iodate. The reduced solution is finally titrated with an N/10 solution of potassium iodate, stoppering the bottle and shaking after each addition, until the chloroform indicator is decolorised. The fully titrated solution has a rose or red colour due to Mo_2O_5. The blank correction is 1 drop of N/10 iodate. Oxidation to MoO_3, although negligibly slow in diffused daylight, is more rapid in direct sunlight, which should therefore be avoided.

The iodine monochloride solution used is made by dissolving 10 grms. potassium iodide and 6·44 grms. potassium iodate in 75 c.c. water, adding 75 c.c. hydrochloric acid and 5 c.c. chloroform, and adjusting to faint iodine colour by violent shaking and addition of dilute solutions of iodate or iodide as required. G. C. J.

New Method of Precipitating Platinum Sulphide and Analysis of Platinised Asbestos. V. N. Ivanov. (*J. Russ. Phys.-Chem. Soc.*, 1916, **48**, 527-529; through *J. Soc. Chem. Ind.*, 1917, **36**, 290.)—The addition of mercuric chloride to a platinum solution prior to precipitation of the metal as sulphide facilitates the estimation of platinum and allows of accurate results being obtained, but the bulk of the precipitate is greatly increased and injurious mercury vapour is liberated when the precipitate is ignited. The incomplete precipitation of platinum sulphide under ordinary conditions depends on the formation of a stable colloidal solution of the sulphide, and the author finds that the hydrosol is converted into the insoluble hydrogel if magnesium chloride is present in the solution. The method employed is as follows: A weighed quantity of about 5 grms. of platinum chloride is dissolved in water in a 250 c.c. flask, the solution being made up to volume and mixed· Twenty-five c.c. of this liquid are diluted to about 200 c.c. in a 250 to 300 c.c. beaker, and then treated with a few drops of hydrochloric acid and about 5 grms. of magnesium chloride, either in solution or as crystals, per 100 c.c. of liquid. A rapid current of hydrogen sulphide is then passed through the solution until the latter is saturated, the precipitate adhering to the gas-delivery tube being removed by a piece of filter-paper and the latter dropped into the liquid, which is then boiled until all odour of hydrogen sulphide has disappeared. The platinum sulphide is washed twice by decantation and several times on the filter with water acidified with one or two drops of hydrochloric acid, the wet filter being then charred in a covered platinum crucible and finally ignited in a blowpipe flame. This method gives results in very close agreement with those obtained electrolytically.

In the case of platinised asbestos, this is treated with *aqua regia*, which dissolves the platinum and also sufficient magnesium salts from the asbestos to render subsequent addition of magnesium chloride superfluous. Ten grms. of the asbestos are heated in a large beaker with excess of *aqua regia* (2 parts of hydrochloric and 1 part of nitric acid) on a water-bath until all the black particles disappear from the asbestos and the liquid assumes an orange-yellow colour. The contents of the beaker are carefully poured into a porcelain funnel, the asbestos, which serves as a filtering medium, being washed free from platinum. The filtrate is made up to a litre in a measuring flask, and 100 c.c. of the solution are evaporated three times to dryness with hydrochloric acid on a water-bath. The residue is dissolved in 50 c.c. of hot water containing 5 c.c. of hydrochloric acid, and the silica and any fibres of asbestos filtered off. The filtrate is diluted with water to about 250 c.c., and the platinum precipitated as sulphide, the subsequent procedure being as described above. With a particular sample of platinised asbestos five estimations of the percentage of platinum present gave results varying from 7·72 to 7·75 by the electrolytic method, and from 7·75 to 7·77 by the above hydrogen sulphide method.

Estimation of Potassium as Perchlorate. G. P. Baxter and M. Kobayashi. (*J. Amer. Chem. Soc.*, 1917, **39**, 249-252.)—The authors confirm the conclusion of Davis (ANALYST, 1913, **38**, 47) and of Thin and Cumming (ANALYST, 1915, **40**, 296) that Davis's modification of the perchlorate method, in which strong alcohol saturated with potassium perchlorate is used to wash the precipitate, is highly accurate. They point out that where the ratio of sodium to potassium is high, the first precipitate may contain sodium, but this can readily be eliminated by washing the precipitate once or twice by decantation with a saturated solution of potassium perchlorate in alcohol, dissolving it in a little water, and evaporating once more after addition of a little perchloric acid. The authors use a platinum sponge crucible and dry at 200° C. in an electric oven, whereas Davis used tared filters and dried at 100° C.

G. C. J.

Titration of Some Bivalent Metal Sulphates by the Conductivity Method. H. S. Harned. (*J. Amer. Chem. Soc.*, 1917, **39**, 252-266.)—Much sharper end-points are obtained by the use of barium hydroxide than by the use of sodium hydroxide, for, when barium hydroxide is used, the conductivity falls very much more rapidly until the end-point is reached, so that the change to increasing conductivity at the end-point is much more marked. The use of barium hydroxide involves titration out of contact with air, for which purpose a suitable cell is described and illustrated in the paper. Any free sulphuric acid in the solution to be titrated is readily neutralised by means of barium hydroxide and a suitable indicator (phenolphthaleïn) before commencing the titration proper. The method affords a convenient and accurate means of estimating magnesium in presence of calcium. Copper must be titrated at a boiling temperature, or oxysulphates separate and low results are obtained. The method is less exact for nickel and cobalt, owing to the difficulty in neutralising solutions of nickel and cobalt salts without precipitating nickel or cobalt hydroxide. The best modification devised by the author gave results about 3 per cent. low with these metals. Cadmium appears to form a stable oxysulphate which makes the method inapplicable.

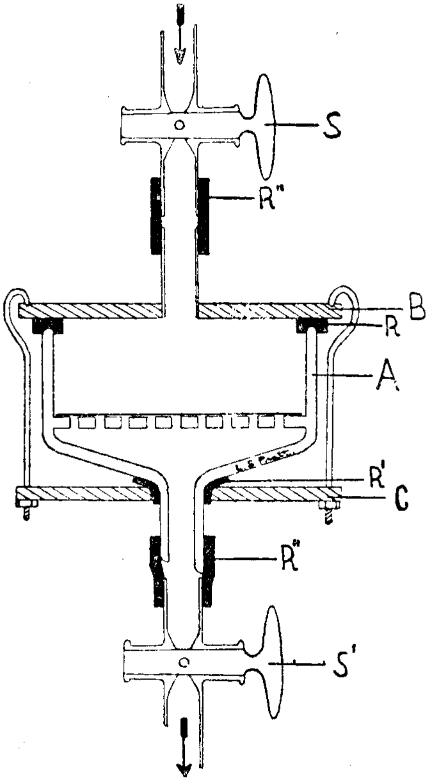
G. C. J.

Interference of Thiocyanates, Ferrocyanides, and Ferricyanides in the Detection of Iodides with Palladium. L. J. Curtman and B. R. Harris. (*J. Amer. Chem. Soc.*, 1917, **39**, 266-270.)—Kern (*Chem. News*, 1875, **32**, 242; 1876, **33**, 184) called attention to the interference of thiocyanates, ferrocyanides, and ferricyanides with the precipitation of iodides as palladium iodide, but he supplied no quantitative data.

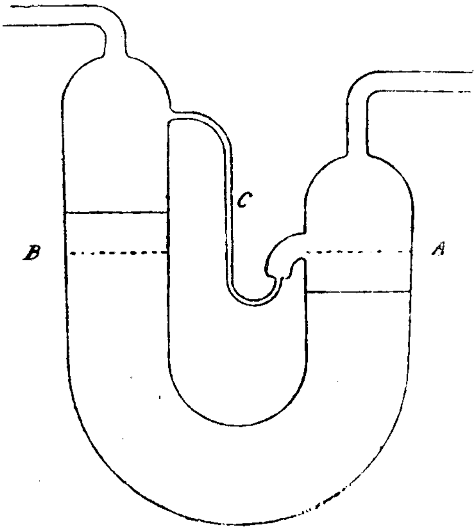
Whereas, in absence of interfering substances, 1 mgrm. of potassium iodide in 5 c.c. of solution gives a distinctly visible black precipitate in a transparent light brown mother liquor, in presence of 5 mgrms. of thiocyanate not less than 5 mgrms. of iodide can be detected with certainty, owing to the precipitation of reddish flocculent palladious thiocyanate. Similarly, 10 mgrms. of thiocyanate will mask any quantity of iodide much less than 10 mgrms. The interference of ferrocyanides and ferricyanides is even greater if the test be made in the cold, but can be greatly diminished by boiling the solutions for fifteen to thirty seconds about ten minutes after the addition of the reagent. Under these conditions, ferrocyanides and ferricyanides interfere with the test less than thiocyanate. G. C. J.

APPARATUS, ETC.

Desiccator for Drying by Means of a Current of Air. L. S. Pratt. (*J. Amer. Chem. Soc.*, 1917, **39**, 271-273.)—The apparatus consists of a Büchner funnel connected below, through cock *S′*, to a safety flask, which in turn is connected with a pump. Resting on the funnel is a heavy brass disc, *B*, on the lower surface of which is cemented a ring or sheet of rubber, *R*, to make a tight joint. Pressure is brought to bear on the disc by means of three screws acting between the disc and a metal collar, *C*. Heavy rubber tubing, *R′*, prevents the collar from exerting unequal pressure on the funnel. In the centre of the disc is set a brass tube, to which is attached, by means of heavy rubber tubing, *R″*, the cock *S*. This cock is further attached to a system of drying-bottles or towers. The material to be desiccated is either filtered into or placed in the funnel. G. C. J.



Laboratory Gas Meter. E. G. Beckett. (*J. Soc. Chem. Ind.*, 1917, **36**, 52.)—The apparatus consists of a U-tube, the two arms of which are connected by a siphon tube, *C*. It is filled with water up to the level shown by the dotted line in *A* and *B*. The gas to be measured enters the limb *A*, and forces the water up into *B*, until the difference in pressure empties the siphon *C* into *B*, and allows the gas to pass from *A* through the siphon into *B*. This re-adjusts the level of the water, which again fills the siphon tube, and the process starts again. Each discharge of the siphon corresponds with the passage of a definite quantity of the gas, but the amount varies with the velocity of the gas. For example, an apparatus which had a capacity of 44·5 c.c. when the gas was introduced at a rate of 15·5 c.c. per second, showed 40·0 c.c. with a velocity of 6·56 and 35·4 c.c. with a velocity of 0·54 c.c. per second. The apparatus is particularly suitable for the measurement of corrosive gases, whilst by substituting some other mobile liquid for water it can be used with soluble gases.



C. A. M.

LAW REPORT.

JONES *v.* ROBINSON.

THIS case came before Mr. Justice Astbury in the Chancery Division of the High Court on Friday, March 2.

The action was brought by the Plaintiff, Mr. G. Cecil Jones, F.I.C., A.C.G.I., Analytical and Consulting Chemist, of 43, Great Tower Street, E.C., against the Defendant, Mr. Grant Robinson (trading as Butcher's Dairies), of 12, Victoria Street, St. Albans, and came before the Court on motion for an interim injunction to restrain the Defendant and his servants and agents from the publication of a certain printed document purporting to be a copy of a report upon a sample of milk analysed by the Plaintiff containing statements which did not form part of the Plaintiff's actual report, and which were not in accordance with the facts.

Mr. Dighton Pollock (instructed by Messrs. Forbes and Son) appeared for the Plaintiff, and Mr. J. E. Harman (instructed by Messrs. Sharpe, Pritchard and Co.) for the Defendant.

Mr. Dighton Pollock said that the Plaintiff had at the request of the Defendant analysed a sample of milk, and had issued to the Defendant a written report upon it. The Defendant had printed and circulated a document purporting to be a copy of a report of the Plaintiff, but containing words and figures which were not in the original, and which the Plaintiff alleged were not correct and the publication of which over his signature was calculated to damage his professional reputation as a Consulting Analyst.

Mr. Harman, on behalf of the Defendant, expressed his client's regret for what had been done, and stated that the alteration of the Plaintiff's report had been made by someone in his employment and without his knowledge. The Defendant would consent to the injunction, and to pay the Plaintiff's costs of the action, and to an inquiry as to damages on the usual terms.

The motion being treated as the trial of the action, his Lordship granted the injunction claimed, ordered the Defendant to pay the Plaintiff's costs, and directed an inquiry to be held as to the damages sustained by the Plaintiff.

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INSTITUTE OF CHEMISTRY.

THIRTY-NINTH ANNUAL GENERAL MEETING.

The Thirty-ninth Annual General Meeting of the Institute of Chemistry was held yesterday at Russell Square, Sir James J. Dobbie, President, in the Chair.

In the course of his Address, the President referred to the services of professional chemists in connection with the War. The high rank which many of the Members and Students had attained and the distinctions they had won gave the Institute every reason to be proud of the part they had taken in the conflict. The Institute had acted as a chemical clearing-house, assisting public departments and firms engaged on Government work to obtain the chemical service they required. Apart from that, the researches on glass initiated by the Institute, particularly the work of Professor Herbert Jackson, had proved of great value, and had been specially recognised by the President of the Board of Trade. Progress had also been made with raising the fund for the new premises of the Institute, for which a further sum of £2,250 was yet required.

In mentioning the losses sustained by British chemistry during the year, the President referred especially to Sir William Ramsay and his work on rare gases, and Mr. David Howard, Past-President, one of the leaders of British chemical industry.

After indicating a number of new industrial developments which called for the help of practical chemists, the President advocated the extension of the training of chemists, particularly in higher physics and physical chemistry, and, therefore, the adoption of a four instead of a three years' course. He emphasised the importance of mechanics to chemists who intended to practise in industry, and recommended a training as wide as possible for chemists generally. Dealing with the recent discussions on general education and the reform of the school curriculum, he criticised what was termed "generalised science," by which he supposed was meant a composite course, including a little physics, a little chemistry, a little biology, and a little of everything else, and suggested that school science should be as simple as possible, and that the first place should be given to mechanics experimentally treated, as being essential to the study of all other experimental science.

The Officers and Members of Council for the ensuing year were duly elected.

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REVIEW.

THE BACTERIOLOGICAL EXAMINATION OF FOOD AND WATER. By W. G. SAVAGE, Cambridge University Press, 1916. Price 8s. net.

While the bacteriological examination of water has been fully treated in numerous textbooks, there has hitherto been no English work dealing with the bacteriological investigation of the commoner articles of food. The present book admirably fills the gap, and, though confined within modest limits, deals in a thoroughly practical manner with the subjects within its scope.

The first two chapters discuss the objects with which water and the various foods have to be investigated and the general methods in use for the identification and detection of " indicator " organisms; following which come sections on water, soil and sewage, shell-fish, milk and its products, meat and meat preparations, air, and, finally, the determination of germicidal and antiseptic power.

The media recommended, or which are in common use, are described in an appendix, and there is an addendum bringing this, which is the second edition, up to date.

A general acquaintance with bacteriological technique on the part of the reader is assumed, but the practical details of the methods employed are set forth clearly and fully enough to satisfy the most exacting.

The author is no bacteria-maniac, and fully recognises the limitations of bacteriological examination. Thus, in the case of water, he points out the absolute necessity of taking into consideration all the other factors bearing on the problem, such as the source and its surroundings, the results of chemical analysis, etc., and very properly insists on the danger of drawing conclusions from isolated bacteriological examinations.

It is satisfactory to find also that he gives no countenance to that slovenly technique which is adopted in some academic laboratories, and may be attributed to a large extent to the fact that bacteriology has fallen into the hands of the medical man, instead of those of the chemist, whose training and experience in delicate manipulation render him much better fitted for work which demands such scrupulous attention to minute details.

The chapter dealing with bacterial food infections and food-poisoning, although very short, is an excellent statement of the present condition of our knowledge of this still somewhat controversial subject, and we entirely agree with the author's suggestion that the term " ptomaine-poisoning," so useful to the medical man in difficulties, " should be abandoned as incorrect and misleading."

Dr. Savage is equally emphatic in his caution as to the value of the determination of antiseptic and germicidal power, though we think he might have gone even further in making clear the fundamental weakness of all the processes hitherto suggested, in so far as they seem tacitly to assume that what is sauce for the goose is sauce for the gander—*i.e.*, that different organisms are affected in the same way by the same antiseptics. The varying degrees of susceptibility of different organisms and of different strains even of the same organism, together with the influence of the foreign substances with which, under the conditions of actual practice, the organisms are necessarily mixed, must tend in many cases to rob laboratory determinations of any value whatever.

The book as a whole is very clearly written, excellently arranged, and well printed and illustrated, though some of the illustrations, such as that of a row of bottles and a pipette, might well have been dispensed with. It contains numerous references to recent literature, and should prove of great value to all concerned with the subject with which it deals.

C. H. CRIBB.