

# THE ANALYST.

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## OBITUARY.

### SIR WILLIAM RAMSAY.

At the western side of the old Andersonian University in George Street, Glasgow, on the place now occupied by the palatial building of the Glasgow and West of Scotland Technical College, there stood a dingy house, the Young Laboratory of Technical Chemistry. The chair was held by a professor of what would to-day be called "hostile alien origin," a very kindly man, whose chief qualifications for a Scotch professorship of technology were that he had to struggle with the language and was not greatly versed in technology. His private assistant from September 6, 1872, was the writer, whose knowledge of the English language was still far more circumscribed, necessitating frequent reference to a dictionary in the middle of a conversation. There were about twenty students in the laboratory, who smiled in the most friendly manner while professor and assistant made themselves freely misunderstood. It was a relief when, at the end of September, a Scotch assistant was engaged for the laboratory tuition of the students. William Ramsay had just arrived from Tübingen, where he had studied organic chemistry, physics, and geology, and obtained the Ph.D. degree by a dissertation on the Toluylic Acids.

Born in Glasgow in 1852, he studied at the University from 1866 to 1869, and entered in the latter year the laboratory of our esteemed Past-President, Dr. R. R. Tatlock, where for a year he was entirely occupied with analytical work. The influence of that year upon Ramsay is shown by the fact that his first appearance as an author was as translator of a little book by Beilstein on Analytical Chemistry, while almost his last consisted in the elaboration of the method for determining dissolved oxygen in water and effluents, in his function as a member of the Royal Commission on Sewage Pollution. Much of his exquisite manipulative skill may be traced to his work under Tatlock.

His grandfather was a dyer, and afterwards chemical manufacturer, producing pyroligneous acid and various acetates, potassium bichromate and Prussian blue, or, rather, the ferro-ferri cyanide known as "Turnbull's blue," which had been discovered by Ramsay's grandfather, whose factories, or perhaps those that in course of time had taken their place, W. Ramsay took pride in showing. His father was an engineer under Robert Napier; his mother, the daughter of a physician with strong chemical leanings. His uncle, Sir Andrew Ramsay, was the Director of

the Geological Survey in succession to Murchison. Ramsay himself attributed his scientific gifts to inheritance from his ancestors. His kindly silent father and his most gentle and saintly mother, who showed me innumerable acts of kindness while I had upon me the homesickness of a youngster who, prior to his emigration to Scotland, had never left the parental house, I hold in affectionate and reverend memory.

I spent many evenings at their home, where William enlivened the company with songs, which in later years were greeted with enthusiastic applause by his students at social evenings of the University College Students' Club—"Marlborouk s'en va-t-en guerre," and such-like. He had a very good voice, played his own accompaniments, and was an expert whistler. He spoke German fluently, with occasional comic lapses, which I endeavoured to correct, in return for services rendered to me by his rough-hewing my efforts in English. He took lessons in conversational French, and, I think, in Italian, and in later years was able to address meetings almost equally well in the four languages. He also had some knowledge of Dutch.

William Ramsay soon became my intimate friend. We were both full of enthusiasm, and, as neither of us could obtain advice or stimulus from our professor, we were thrown upon our own resources and mutual help. Our daily conversations turned largely, apart from matters arising out of our immediate duties, round philosophical questions, renewed occasionally in later years. On his side, he was naturally influenced by his inheritance from Covenanting ancestors; I, on mine, by that from unorthodox and agnostic surroundings. As far as I am concerned, these most friendly conversations affected the whole of my more mature opinions. Chemically our life at the Andersonian was unsatisfactory. The students scoffed at the professor, and we felt hurt at our association with him. As a consequence we both freed ourselves as soon as practicable from our engagements.

He in 1874 entered into the serene and healthy atmosphere of the Glasgow University, and had the good fortune to continue his academic career and to occupy himself with genial work and investigations. I, unluckily, jumped out of the frying-pan into the fire by accepting an engagement as assistant to a physician who passed among a section of the public as a great chemist upon the strength of his possession and intelligent use of a microscope. While the professor had to ask his assistants for help in writing out the formula showing the action of hydrochloric acid upon metallic iron, my later employer required information as to the composition of quartz and such-like.

At the Andersonian we were confronted for the first time with the working of the simple mercury Sprengel pump, which in its later developments became so important an instrument in Ramsay's epoch-making discoveries.

As assistant to Professor Ferguson from 1874 onward, Ramsay lectured mainly on inorganic chemistry, and in 1880 became Professor, and soon afterwards Principal, of University College, Bristol. He relates how his knowledge of the Dutch language helped him to this post, one of the Governors of the College, a clergyman, being most favourably impressed by Ramsay's ability to translate some theological pamphlets written in Dutch, which he had just received, but was unable to decipher.

In Bristol he worked mainly on questions of critical pressures and temperatures, molecular volumes, and many other allied physico-chemical problems. In 1887 he became Williamson's successor at University College, London, and occupied this post till his retirement a year ago.

It is not my intention here to write a history of Ramsay's work. This passed before the eyes of the whole chemical world, and affected and revolutionised scientific thought. The work done at Bristol formed, as it were, the preliminary training for the researches which culminated in the discovery, in 1894, of the family of inert gases, and of emanations, and led to experiments on the mutability of elements.

It is, of course, known to everybody that Lord Rayleigh had observed, early in 1894, that the specific gravity of nitrogen derived from the air was greater than that produced chemically. The explanation of this difference was entirely due to Ramsay's industry, Lord Rayleigh having published in *Nature* the fact observed by him, and asking the readers to assist him in finding the cause.

I count it an honour to have remained in constant touch and correspondence with Ramsay during the whole of his active life, to have been shown privately many of the phenomena and substances discovered and investigated by him, and to have received dedicated copies of almost all the papers he contributed to scientific literature. He always took an almost boyish delight in showing or repeating his experiments, and he often reminded me of Faraday's simplicity, who, we are told, was wont, when showing to Royal Institution audiences new phenomena in electricity, to turn to them with the appeal, "Now, isn't it beautiful!" To this simplicity in Ramsay's character is attributable the fact that, after his name had become a household word, he was occasionally "taken in" by plausible promoters, who hoped to obtain his support for schemes to extract gold—from the public.

Of his technical work, apart from his strictly scientific work, little is known to the outside world; but, as I have been associated with him on many occasions, I may be permitted to refer to some of this. He was an admirable witness before High Courts and Parliamentary Committees, and his help was, naturally, in great request.

A town on the East Coast required an extension of its water-supply. Deep wells were not available, and after much thought and experiment Parliamentary sanction was asked for the abstraction and use of river water, under proper conditions of storage, and safeguarding from pollution. A spot had been selected for the intake as far as possible removed from all danger. Shortly before the Parliamentary inquiry took place there occurred a remarkable catastrophe. Long-continued easterly storms (during which the G.E.R. steamer *Berlin* was wrecked at the Hook of Holland) drove the sea-water inland far beyond any point which it had reached "within memory of living man," and the river at the proposed intake became temporarily brackish. The Parliamentary Committee, in consequence, refused to sanction the scheme until means could be found to prevent the town supply from becoming mixed with sea-water. Ramsay and I collaborated in the construction of devices intended to announce automatically the arrival of sea-water some miles below the intake and the closing of the valves. We brought two plans before the Committee during the next session, one being based upon the altered electric

resistance, another upon the change in specific gravity, of the river water. These the Committee deemed efficient, and gave its sanction to the proposed extension, this being the first occasion, after an interval of many years, on which river water was allowed to be used as a public supply.

Coolgardie Goldfields are situated in a waterless district, more than three hundred miles from the sea. The Government of Western Australia had constructed at enormous expense a pipe line of thin steel, supplying an adequate quantity of good water from the neighbourhood of the coast. Unfortunately, it was found that after a few years the corrosive action of the water on the steel pipes began to obstruct and perforate these, the whole structure becoming endangered. The Government instructed the eminent engineer, Dr. G. F. Deacon, Sir William Ramsay, and the writer, to inquire into the subject and to devise means of arresting the corrosion. We arrived at the conclusion that owing to the construction of the line, which naturally ran up hill and down dale, the water became charged at a number of reservoirs with oxygen, and that the oxygen thus introduced at intervals was the prime cause of the trouble. Several modes of removing the oxygen and preventing its reintroduction into the supply were considered. Ramsay constructed a most ingenious device for pumping out the dissolved air from the water, and installed at University College an experimental plant, working continuously and at very small cost, supplying water in which bright steel bars remained absolutely untarnished for weeks.

In an entirely different field his assistance was of great help in a law case which aroused much public interest—namely, the litigation concerning the composition of ritual wax candles for use in Roman Catholic churches. The questions involved were quite outside his proper work, but perhaps on that account he took all the greater pleasure in their elucidation.

The work he did as a member of the Royal Commission on Sewage Pollution, sitting for many years after 1898, most materially helped to solve the problem of sewage purification, which had been one of the most urgent from the middle of last century.

Ramsay was always proud of his Scottish descent, and his name will ever be counted as one of the foremost of the many Scotsmen who have helped in the rearing of the edifice of modern science. Scotland's sons who have thus contributed are numerous out of proportion to its population, and surely thus exceed those of any other country in the world. They did fundamental work: Hume, Hutton, James Watt, Thomas Graham, Thomas Thomson, William Thomson (Lord Kelvin), James Dewar, William Ramsay.

From the long-ago time of 1872, to his death on July 23, 1916, I always found him the same kindly, upright, joyous friend, unspoiled by his successes and by the honours which were heaped upon him by scientific societies, academies, and Governments.

A few years ago he recurred to our early philosophical discussions, and wrote to me :

“I think I have found the answer. It is in a book by Jerome K. Jerome; here is the quotation :

“ ‘What do you believe,’ I asked—‘father, really, I mean?’ The night had fallen. My father put his arm round me, and drew me to him.

“ ‘That we are God’s children, little brother,’ he answered—‘that what He wills for us is best. It may be life; it may be sleep; it will be best. I cannot think that He will let us die; that were to think of Him as without purpose. But His uses may not be our desires. We must trust Him. Though He slay me, yet I will trust Him.’

“ We walked in silence before my father spoke again:

“ ‘Now abideth these three: faith, hope, and charity. You remember the verse—faith in God’s goodness to us, hope that our desires may be fulfilled; but these concern but ourselves—the greatest of all is charity.’

“ ‘Be kind—that is all it means,’ continued my father. ‘Often we do what we think right, and evil comes of it, and out of evil comes good. We cannot understand; maybe the old laws we have misread. But the new law, that we love one another—all creatures He has made—that is so clear. And if it be that we are here together only for a little while, the future dark, how much the greater use have we of one another!’ ”

And Ramsay summed up: “That appears to me about the sum of the whole matter.”

May I, lastly, quote a few words written to me by Lady Ramsay, after death had released the good and noble man from terrible suffering?—

“One of the attractions of his retirement was that he hoped to see his old friends in the quiet of the country; but it was not to be. The war made it impossible. And then came the weary illness. The way he bore the suffering, and what to him was worse, the inaction, was truly heroic. It did one good to be near him.”

To-day people belonging to almost all the European nations are killing each other; yet it is true that the world is better for having had Ramsay.

OTTO HEHNER,



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

### THE APPLICATION OF THE METHOD OF CONSTANT BOILING-POINT MIXTURES TO THE QUALITATIVE ANALYSIS OF CERTAIN MIXED ORGANIC LIQUIDS.

BY W. R. G. ATKINS, SC.D.

THE present paper is an attempt to illustrate the usefulness of distillation methods for qualitative analysis. In certain cases it is also a most reliable means of quantitative analysis, as may be seen by reference to Young's "Fractional Distillation."

In the course of some recent work it was necessary to make analyses of rather complex mixtures of organic liquids—commercial solvents and so forth. A preliminary qualitative analysis was made on the following lines: In organic analysis it is customary to determine the boiling-point of a liquid after purification as a means of identification. But such purification is frequently difficult, or impossible in the case of certain mixtures when the quantities are small. It is often possible, however, to add another liquid with which the unknown liquid will form a mixture of constant boiling-point, and so to identify a small amount of it in a mixture. A list of such mixtures, their boiling-points and compositions, may be found in "Fractional Distillation." Data concerning more recently discovered mixtures may be found in the "Tables Annuelles de Constantes et Données Numériques."

To carry out the analysis a small round bottomed flask is fitted below a Young's "evaporator" still head. One of eight-sections was used, but a five-section head would suffice for most purposes. The contents of the flask are heated with a small naked flame. If the amount of liquid in the flask is to be reduced to a small volume towards the end of the distillation it is advisable to have a thin wisp of cotton wool wound round the bulb of the thermometer. The thread of the mercury should be in the vapour as far as possible. In some of the recently manufactured English made still-heads of this type the length above the top section and below the side tube is too short, and not in accord with the original design.

The following examples of the application of this method may be given:

It was desired to ascertain the composition of a liquid smelling of alcohol. A small quantity of benzene, free from thiophene and redistilled till pure, was added to the mixture and the whole carefully distilled at a rate not exceeding sixty drops a minute, usually at about forty per minute. The thermometer rose rapidly to the neighbourhood of the boiling-point of the binary mixture of methyl alcohol and benzene ( $58.35^{\circ}\text{C}$ .), and halted at about that point for some time. Thus the presence of methyl alcohol was established. There was another slight halt at about  $64.8^{\circ}\text{C}$ ., a slight turbidity appearing in the column, followed by a rise to the region of

68.25° C., at which a good quantity came over. The thermometer then rose to about 78.3° C. Thus, there is no doubt that the other constituent of the mixture was ethyl alcohol with a trace of water, for the halts were at the boiling-points of the mixtures, ethyl alcohol, water, benzene, and ethyl alcohol, benzene, and finally at that of ethyl alcohol.

Another sample already contained some benzene, so the points of arrests were obtained without its addition.

The presence and approximate amount (about 2 per cent.) of water in commercial methyl ethyl ketone were also ascertained by distillation. There was a halt at the boiling-point of its binary mixture with water, and the fraction up to the middle point between this and that of the pure liquid was collected and weighed. Since the composition of the mixture was known, the amount of water could be calculated.

Again, the presence of a small amount of methyl ethyl ketone in a mixture of acetone and benzene was shown by distilling off most of the acetone, and adding a little water. A small fraction was collected at about 73° C., the boiling-point of the constant boiling mixture of the ketone and water, and thus its presence was demonstrated. It may be mentioned that the ketone forms another constant boiling mixture, of as yet unknown composition, with benzene. This, however, boils at a temperature so close to the boiling-point of the pure ketone that it could not be used to detect the presence of a small quantity with any degree of certainty. Since the qualitative reactions of acetone and its next higher homologue are so much alike, I am not aware of any other method by which the presence of the trace of the higher ketone could be detected.

Thus, by the addition of water, benzene, or both of them, the presence of many alcohols in mixtures can be ascertained. No doubt other liquids may be added also, as the range of substances investigated increases. An additional advantage of the method is that when only a small quantity—*e.g.*, 1 or 2 c.c.—of liquid is available, a distillation can be made by diluting largely with water, benzene, alcohol, or other suitable liquid. Also where a ternary mixture distils over the percentage of alcohol is usually small, and so in quantitative work errors, due to evaporation and drainage losses, are minimised. In qualitative work the increased volume of the distillate prolongs the arrest in the thermometer readings during distillation at a uniform rate, and so renders the test more delicate. These references illustrate the usefulness of the method; applications in individual cases will easily suggest themselves. Its special utility lies in the study of mixtures of homologous series, in which the ordinary qualitative reactions frequently offer but little help.

UNIVERSITY CHEMICAL LABORATORY,  
TRINITY COLLEGE, DUBLIN.



## THE EFFECT OF FEEDING ON THE COMPOSITION OF BUTTER: DECORTICATED GROUND NUT CAKE AND DECORTICATED COTTON CAKE.

By HAROLD T. CRANFIELD.

In the spring of this year a feeding experiment was designed and carried out at the Midland Agricultural and Dairy College, comparing the value of ground nut cake against decorticated cotton cake as a food for dairy cows, and in this paper is given the effects of these feeding stuffs on the composition of butter made from the milk produced during this experiment.

Ground nut cake (also called earth nut cake) is the residuum from the extraction of arachis oil which is obtained from the ground nut, *Arachis hypogaea* (also known as earth nut, monkey nut, or pea nut). The plant from which this nut is obtained is subtropical, and flourishes in many parts of the world. The bulk of the nuts are exported from India, Nigeria, Gambia, Senegal, and China. Previous to the war ground nuts were chiefly imported by Germany and Holland, and to a lesser extent by France, but during the last two years a large quantity has been diverted to English ports, and English-made cake is now appearing on our markets.

The cake has been used extensively for many years on the Continent as a feeding stuff for stock, but only a little obtained access to this country. It varies in colour from white to dark brown, according to the quality of the nuts and method of extraction of the oil, the white and greyish-white cakes being, as a rule, the purest and richest in feeding constituents. The nuts are usually decorticated, but occasionally undecorticated cakes are met with. The latter are high in woody fibre, and therefore very indigestible.

Decorticated ground nut cake is a very palatable food, having a pleasant taste and smell, and is relished by stock. The only likely impurities in the cake are excessive dirt and castor oil seeds. Up to the present time it has been one of the cheapest concentrated cattle foods on our markets during the past two years.

The analyses of the two cakes used in this experiment are as follows:

				Decorticated Ground Nut Cake.	Decorticated Cotton Cake.
Moisture	..	..	..	10.62	9.27
Oil	..	..	..	7.55	12.89
Proteins	..	..	..	42.96	39.37
Soluble Carbohydrates	..	..	..	23.76	24.45
Fibre	..	..	..	9.62	7.15
Ash	..	..	..	5.49	6.87
				<hr style="width: 50%; margin: 0 auto;"/> 100.00	<hr style="width: 50%; margin: 0 auto;"/> 100.00
Total food units	..	..	..	149	155

**EXPERIMENTAL DETAILS.**—These were on the lines of the previous feeding experiments—viz., four carefully selected cows in each set (ANALYST, 1915, 40, 433). The cows were receiving all their food in stall, and their rations were as follows:



DAILY RATION PER COW.

First and Second Weeks :

	Set A.		Set B.
Basal Ration.	{	56 pounds mangels.	56 pounds mangels.
		14 „ long hay.	14 „ long hay.
		5 „ chopped hay.	5 „ chopped hay.
		1 pound bran.	1 pound bran.
		$\frac{1}{2}$ „ dried yeast.	$\frac{1}{2}$ „ dried yeast.
		4 pounds decorticated ground nut cake.	4 pounds decorticated cotton cake.

Third Week (Transition Period).—Set A received a diminishing quantity of ground nut cake and an increasing quantity of cotton cake; Set B *vice versa*.

Fourth and Fifth Weeks.—Set A received the basal ration *plus* 4 pounds of decorticated cotton cake, while Set B were fed with the basal ration and 4 pounds of decorticated ground nut cake.

Proportionate samples of the mixed milk from each set of cows were taken night and morning on alternate days. These samples were separated and the cream churned after ripening with starter. Butter fat was prepared in the usual way from the butter, and subjected to analysis.

AVERAGES.

Reichert-Meissl Value :

			First and Second Weeks.	Fourth and Fifth Weeks.
Set A	..	..	32.32	30.28
Set B	..	..	31.13	29.29
Set A.		Set B.	From Ground Nut Cake.	From Cotton Cake.
31.30		30.21	30.80	30.70

AVERAGES.

Kirschner Value :

			First and Second Weeks.	Fourth and Fifth Weeks.
Set A	..	..	23.60	23.40
Set B	..	..	24.22	22.01
Set A.		Set B.	From Ground Nut Cake.	From Cotton Cake.
23.50		23.11	22.80	23.81

AVERAGES.

Polenske Value :

			First and Second Weeks.	Fourth and Fifth Weeks.
Set A	..	..	1.93	1.87
Set B	..	..	1.89	1.96
Set A.		Set B.	From Ground Nut Cake.	From Cotton Cake.
1.90		1.92	1.94	1.88

AVERAGES.

Refractometer Figure (35° C.):

			First and Second Weeks.	Fourth and Fifth Weeks.
Set A	..	..	45.93	46.93
Set B	..	..	45.93	47.11
Set A.		Set B.	From Ground Nut Cake.	From Cotton Cake.
46.43		46.52	46.52	46.43

It will be seen from the above figures that the differences obtained in the four determinations are very small. One may therefore conclude that these values were not influenced by the change of food.

In spite of the uniformity of these figures, there appeared to be some difference in the composition of the two sets of butters, one set (ground nut) having a much lower solidification point than the other set. The ground nut butter was also considerably softer than the cotton cake butter. This pointed to a possible variation in the percentages of unsaturated fats.

*Iodine Absorption Value.*—Through the kindness of Mr. H. D. Richmond, I was able to obtain the iodine absorption figures of several of the samples, and the results of his determinations are as follows:

## SECOND WEEK.

Sample No.	From Ground Nut Cake.	Sample No.	From Cotton Cake.
A5 .. ..	40.95	B5 .. ..	39.0
A6 .. ..	39.8	B6 .. ..	38.8
A7 .. ..	40.55	B7 .. ..	38.4
Average ..	40.4	Average ..	38.7

## FIFTH WEEK.

Sample No.	From Ground Nut Cake.	Sample No.	From Cotton Cake.
B16 .. ..	43.6	A16 .. ..	43.3
B17 .. ..	43.8	A17 .. ..	43.3
B18 .. ..	43.1	A18 .. ..	43.4
Average ..	43.5	Average ..	43.3

These figures are very curious. In the second-week samples we have a marked increase in favour of the ground nut cake, this corresponding with the low solidification point and the softness of the butter, but in the fifth week the variation is much smaller—in fact, the averages are almost identical.

*Potash Absorption and Saponification Equivalent.*—I subsequently made determinations of these values on a few of the samples, but both gave normal figures, and no great variations were indicated.

## GROUND NUT.

Sample No.	Potash Absorption.	Saponification Equivalent.
A4 .. ..	230.1	243.8
A6 .. ..	231.4	242.4
B16 .. ..	228.6	245.4

## COTTON.

Sample No.	Potash Absorption.	Saponification Equivalent.
B4 .. ..	228.6	245.4
B6 .. ..	230.1	243.8
A16 .. ..	230.1	243.8

The averages of these figures are practically the same.

*Specific Gravity at 100° F.*—Determinations were made on four of the samples by means of a pycnometer, and the results are as follows:

## GROUND NUT.

Sample No.	Potash Absorption.	Average.
A7 .. .. .	0.9145}	0.9138
B17 .. .. .	0.9131}	

## COTTON.

Sample No.	Potash Absorption.	Average.
B7 .. .. .	0.9140}	0.9138
A17 .. .. .	0.9136}	

None of these estimations appear to explain conclusively the difference in softness of the two sets of butters, but the supply of fat being exhausted, I was unable to continue the investigation.

*Quality of the Butter.*—Throughout the experiment it was found that the cream from the cotton cake-fed cows took a much longer time in churning than the ground nut samples.

The ground nut butters were much softer than the cotton butters. As regards flavour no great differences were noticeable, all samples being quite good.

The ground-nut butters were, as a rule, rather darker in colour than the cotton-seed butters.

CONCLUSIONS.—No great differences are apparent in the composition of butter fat produced in this feeding experiment except in the proportion of unsaturated fats, which appear to be rather greater in the samples of butter produced from the ground nut cake feeding.

Decorticated ground-nut cake is an excellent food for butter production, but is more suitable for winter feeding, in consequence of the softness of the butter produced.

Decorticated cotton cake produces a firm butter of good quality, and is therefore more suitable for summer feeding.

I wish to express my best thanks to Mr. H. D. Richmond for help and advice; to Miss B. Manners for superintending the churning of the butter samples; and to Mr. J. Dunlop for facilities in the collection of the samples of milk.



## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

## FOOD AND DRUGS ANALYSIS.

**Physical and Chemical Characters for the Identification of Aspirin. D. E. Tsakalotos.** (*J. Pharm. et de Chim.*, 1916, **14**, 174-177.)—Aspirin crystallises in small well-characterised prisms. When heated over a flame on a glass slide up to but not beyond the melting-point, resolidification takes place, not in the form of prismatic crystals, but as concentric rings about round centres, the successive rings outwards being of increasing thickness. When heated to a temperature distinctly above the melting-point and cooled very gradually, solidification takes place in the form of a transparent vitreous mass. Fusion takes place with decomposition and liberation of acetic acid; consequently, no definite melting-point can be given for aspirin; observations range from 125° C., or even lower, up to 135° C., depending on the rate of heating. On heating for 1 hour at 130° C., the loss of acetic acid corresponds to the conversion of 66 per cent. of the aspirin into salicylosalicylic acid. With an aqueous solution of pure aspirin, freshly prepared, ferric chloride gives no coloration; but if the aspirin be heated to incipient fusion and then dissolved, the addition of a few drops of ferric chloride gives an intense violet coloration. When aspirin is heated above its melting-point and then dissolved in alcohol, the addition of water produces a white precipitate of salicylosalicylic acid, and a few drops of ferric chloride added to this gives a whitish-violet coloration. Some specific reactions, according to Self, are given with a vanadic acid reagent. The author prepares this reagent without the addition of formaldehyde, thus: A small quantity of ammonium vanadate is dissolved in concentrated sulphuric acid; an orange colour is produced, and water is added until this colour is weakened but not discharged. With this reagent, pure aspirin in the solid state shows no change at first, but in a short time the reagent becomes yellowish-green and finally an intense green. Aspirin previously heated to incipient fusion gives an intense green immediately. Aspirin previously heated above its melting-point gives a dark green colour, which immediately changes to brown. J. F. B.

**Estimation of Gum in the Official Syrup of Gum. E. Luce.** (*Ann. Falsific.*, 1916, **9**, 227-231.)—The test of Roussin, depending on the formation of a jelly on the addition of ferric chloride, gives only approximate indications or, if carried out so as to afford quantitative results, is very tedious. Two methods depending on the use of alcohol are more convenient: that of Rocques and Sellier, in which precipitation is performed in presence of lead acetate, is the more exact, while that of Bellier, where calcium chloride is employed, is simpler and sufficiently accurate for practical purposes. According to the method of Rocques and Sellier, 20 grms. of the syrup of gum are heated with 50 c.c. of water in a measuring flask and diluted to 100 c.c. Twenty-five c.c. of the solution are treated with 50 c.c. of 95 per cent. alcohol, with constant stirring, and 2 c.c. of a saturated alcoholic solution of neutral lead acetate

are added drop by drop. The precipitate is allowed to settle for half an hour, the liquid is decanted off through a counterpoised filter; the precipitate is washed by decantation with 50 c.c. of 75 per cent. alcohol in two portions, and transferred to the filter, where it is washed with 20 c.c. of 75 per cent. alcohol, then dried in the oven at 100°-110° C. for six hours. It is weighed dry, incinerated in a porcelain crucible with the paper, and the ash moistened with 10 drops of nitric acid. The residue is weighed as lead oxide, and the weight deducted from that of the precipitate. The final result is multiplied by the factor 1.1764 in order to convert dry ash-free gum into terms of natural gum-arabic. According to Bellier's method, the syrup is diluted in the manner described above, and 20 c.c. of the solution are treated gradually, with stirring, with 40 c.c. of 95 per cent. alcohol and 1 c.c. of a 10 per cent. aqueous solution of calcium chloride. The precipitate is left to settle for twenty-four hours and the liquid decanted off; washing is performed by decantation with 60 c.c. of 65 per cent. alcohol, three times; the precipitate is transferred to the filter, and washed again with 20 c.c. of 65 per cent. alcohol. It is dried in the oven on the counterpoised filter paper and weighed dry. The dry weight, without correcting for ash, is multiplied by 1.1363 for the equivalent of natural air-dry gum. The results are slightly low (about 98 per cent. of the actual). Obviously these methods are only correct with pure gum syrups, free from dextrin. J. F. B.

**Philippine Beeswax.** H. C. Brill and F. Agcaoli. (*Philippine J. of Science*, 1916, 11, 15-18.)—Thirteen samples of genuine Philippine beeswax (which is produced by *Apis zonata*, *A. dorsata*, and *A. indica*) gave the following analytical results after being freed from impurities by boiling with water, and dried at 100° C.:

	Sp. gr. at 15.5° C.	Melt- ing Point. ° C.	Saponi- fication Value.	Acid Value.	Ester Value.	Ratio Num- ber.	Iodine Value (Hanús).	Unsaponi- fied Matter. Per Cent.	Cloud- ing Point. ° C.
Maximum ..	0.9918	64.5	107.0	7.9	100.1	15.6	10.8	58.6	60.0
Minimum ..	0.9309	62.0	96.3	6.0	90.0	12.4	7.4	51.6	59.0
Average ..	0.9601	63.2	101.7	6.8	94.8	13.9	9.0	55.7	59.6

The clouding-point was determined by the method of Salamon and Seaber (ANALYST, 1915, 40, 329). The melting-points are lower, and the saponification, acid and ester values higher than the corresponding values of Japanese and Korean beeswax (*ibid.*, 1915, 40, 343). The percentage of unsaponifiable matter is somewhat higher than the average value (52.38) given by Allen and Thomson for beeswax.

C. A. M.

**Peroxidase Reaction in Milk.** W. Grimmer. (*Milchw. Zentr.*, 1915, 44, 246-247; through *J. Chem. Soc.*, 1916, 110, ii., 403-404.)—The use of guaiacol and ethyl hydrogen peroxide is recommended for the detection of peroxidase in milk, since dilute solutions of these two substances remain stable for several years; they possess,

therefore, a distinct advantage over guaiacum tincture and hydrogen peroxide solution. The test is carried out by mixing a few c.c. of milk with 2 drops of guaiacol solution (1 grm. of guaiacol dissolved in 10 c.c. of alcohol and diluted with water to 100 c.c.) and adding 2 drops of a 0.1 per cent. ethyl hydrogen peroxide solution. Unheated milk yields a brick-red coloration, whilst boiled milk remains colourless. The ethyl hydrogen peroxide may be prepared by the method described by Baeyer and Villiger (*J. Chem. Soc.*, 1916, **110**, I., 308).

**Quantitative Estimation of Morphine in the Various Organs when Injected into Cats and Rabbits.** A. W. Homberger and J. C. Munch. (*J. Amer. Chem. Soc.*, 1916, **38**, 1873-1876.)—Experiments are described which show that over 97 per cent. of the morphine administered hypodermically can be recovered by submitting the kidneys, liver, spleen, stomach, bladder and urine to analysis in the usual manner immediately after death. The proportion contained in the stomach is always small (1 to 3 per cent. of the total), but some is always found there. After 2 months' burial, only 20 to 25 per cent. can be recovered, but from embalmed bodies as much as 70 per cent. can be recovered even after three months. For the analysis of the organs, Autenrieth's modification ("Detection of Poisons," 1915, 57) of the Stas-Otto process was used with Puckner's final extraction by hot amyl alcohol in slightly ammoniacal solution (*J. Amer. Chem. Soc.*, 1901, **23**, 420). For the analysis of blood and urine, Dragendorff's method (Blyth's "Poisons," 1906, 313) was followed again with Puckner's precautions (*loc. cit.*).

G. C. J.

**Tin in Canned Foods.** W. D. Bigelow. (*J. Ind. and Eng. Chem.*, 1916, **8**, 813-815.)—The tin found in canned foods is usually assumed to be in solution, but the separate estimation of tin in the drained solids and in the liquor furnishes evidence that a large proportion of the total tin is present in an insoluble form, some also being present in the colloidal state (Chapman, *ANALYST*, 1913, **38**, 472). The longer the food has been canned, the higher is the proportion of insoluble tin, tin originally in solution being slowly rendered insoluble. Results obtained in the study of the toxicity of soluble tin compounds cannot be used as a criterion of the toxicity of canned foods containing tin in an insoluble form, since in such a form it is probably far less readily absorbed from the intestinal tract (*cf.* Buchanan and Schryver, *ANALYST*, 1909, **34**, 121). A number of analyses are quoted.

H. F. E. H.

### ORGANIC ANALYSIS.

**Estimation of Small Amounts of Alcohol and Water in Ether.** E. Malinekrodt and A. D. Alt. (*J. Ind. and Eng. Chem.*, 1916, **8**, 807-812.)—Regnauld and Adrian (*J. Pharm. et Chem.*, 1864, **45**, 193) determined the percentage of water in mixtures of water, alcohol, and ether from the change in density produced after absorbing the water by potassium carbonate. The authors determined the water directly by weighing the potassium carbonate before and after it had absorbed water

from the mixture, the method being found very accurate and not interfered with by the presence of alcohol, provided that the small amount of alcohol adhering to the potassium carbonate was washed out with anhydrous ether, the carbonate being finally dried at 60° C. For the estimation of the residual mixture of alcohol and ether, tables were made of the densities of such mixtures, elaborate precautions in the way of temperature corrections being taken to ensure accuracy. Test mixtures were made of ether containing 1, 2, 3 and 4 per cent. of alcohol, a sp. gr. curve being constructed from them, the following values being recorded (temp. 25° C., hydrogen scale):

Ether.	Alcohol per cent. by Water.				Sp. Gr.
99	...	...	1	...	0.7110
98	...	...	2	...	0.7121
97	...	...	3	...	0.7130
96	...	...	4	...	0.7141

Market brands of ether intended for anæsthetic purposes showed from 0.12 to 4.2 per cent. of alcohol and from 0.11 to 1.1 per cent. of water. H. F. E. H.

**General Reaction of Alkaloids containing a Phenolic Group (Morphine, Cupreine, Adrenaline, etc.). G. Denigés.** (*Bull. Soc. Chim.*, 1916, 19, 308-311.)

—All phenolic substances give a red coloration with titanous acid in the presence of sulphuric acid, and the author has applied this reaction to alkaloids containing a phenolic group, with the following results: Morphine, blood-red coloration; apomorphine, red-violet; oxydimorphine, wine-red; cupreine, orange (similar to the colour of dichromate solution); hordenine, orange; tyrosine, orange; adrenaline, red-brown. The titanous acid reagent is conveniently prepared by heating a few fragments of native titanous acid (rutile) with sulphuric acid for several hours, cooling the mixture, and decanting the clear solution. The reaction may be obtained with a few hundredths of a milligram of the alkaloids. Proteins also give the reaction owing to the presence of the tyrosine group. W. P. S.

**Estimation of Glycerol in Oils as Sodium Glyceroxide. H. Bull.** (*Chem. Zeit.*, 1916, 40, 690.)—The following modification of a method described

previously by the author (*ANALYST*, 1900, 25, 322) yields trustworthy results for the estimation of glycerol in oils; the essential feature of the modification consists in removing any free fatty acid from the oil, since the presence of fatty acids interferes with the subsequent part of the process. Ten grms. of the oil are placed in a 100 c.c. measuring cylinder, and petroleum spirit is added up to the 100 c.c. mark; 10 c.c. of glycerol-potassium hydroxide solution (20 c.c. of 50 per cent. potassium hydroxide solution, 240 c.c. of glycerol, and 240 c.c. of water) are next added, and the contents of the cylinder are mixed, but not shaken violently. After settling for about eighteen hours, 30 c.c. of the clear petroleum spirit solution are transferred to a 50 c.c. cylinder, 3 c.c. of sodium ethoxide solution (23 grms. of metallic sodium dissolved in 500 c.c. of alcohol) are added, the mixture is diluted to 50 c.c. with petroleum spirit, mixed, and allowed to stand for some hours. The sodium glyceroxide

gradually settles to the bottom of the cylinder, leaving the petroleum spirit clear; if a fine flocculent precipitate remains in the petroleum spirit layer, it may be ignored, as it is not sodium glyceroxide and does not affect the estimation. Twenty-five c.c. of the petroleum spirit layer are then withdrawn, diluted with 10 c.c. of alcohol, and titrated with  $\frac{N}{10}$  hydrochloric acid, using phenolphthalein as the indicator. The remaining contents of the 50 c.c. cylinder are then poured into a flask, the cylinder is rinsed out with about 20 c.c. of alcohol, and the mixture at once titrated. To avoid the use of a large volume of acid in this titration, 5 c.c. of  $\frac{N}{2}$  hydrochloric acid may be added at first, and the titration then completed with  $\frac{N}{5}$  acid. The mixture should be titrated immediately after the addition of the alcohol, in order to prevent saponification of the fatty esters. The difference in the quantities of  $\frac{N}{10}$  hydrochloric acid used in the two titrations is multiplied by 0.0092 to obtain the amount of glycerol present in 3 grms. of the oil. Results of estimations are given, showing that the percentage quantities of glycerol found by the method agree with the amounts calculated from the ester values of the oils examined.

W. P. S.

#### Use of Ammonium Nitrate in Estimating the Calorific Power of Lignites.

**R. Salvadori.** (*Ann. Chim. Applic.*, 1916, 6, 113-114.)—The ordinary empirical formulæ (Mahler's, Gouthal's, etc.) used in calculating the calorific power of coal are not applicable to lignites. This is probably owing to the different character of their volatile constituents, which are not completely combustible, such as, e.g., pyroligneous acid. It would therefore be necessary to introduce into the formulæ a coefficient depending, in the main, on the acidity of the volatile products. As a rule it is not possible to use Thomson's calorimeter for combustibles with a calorific power of less than 5,000. To obviate this difficulty dry ammonium nitrate is added to the mixture of potassium chlorate and nitrate, each gram added increasing the temperature of 2 kilos of water by 0.54° C. The ammonium nitrate is fused and powdered and kept in a desiccator over calcium chloride or phosphoric anhydride. Two grms. of the finely powdered lignite are mixed with 20 grms. of the mixture of potassium chlorate and nitrate (3:1) and 1 gm. of the prepared ammonium nitrate, and the mixture ignited in the calorimeter. Combustion ought to be effected in thirty to forty-five seconds. A deduction of 0.54° C. is made from the observed temperature. Or a mixture of 18 grms. of potassium chlorate and 3 grms. of ammonium nitrate may be used as the combustion agent, and 1.62° C. deducted from the reading.

C. A. M.

#### Analysis of Benzol First-Runnings. P. E. Spielmann and F. B. Jones.

(*J. Soc. Chem. Ind.*, 1916, 35, 911-912.)—The first-runnings differ from the benzol fraction mainly in containing 10 or 15 per cent. (rarely as much as 65 per cent.) of carbon bisulphide, and up to 15 per cent. of paraffin. The method of analysing commercial benzols previously described (*ANALYST*, 1916, 171) is applicable to first-runnings, provided the following modifications be made: (1) *Carbon bisulphide*, when present in high proportion is best estimated by diluting the sample with approximately five times its volume of benzene which has previously been freed from any carbon disulphide. (2) *Paraffin*: The specific gravity of the paraffin of this fraction



is 0.700. If it is present in such proportion as to lie outside the graph given in the paper, it may be estimated by means of the benzol graph. The difference between the sp. gr. of the benzene-toluene mixture thus found and that of the sample freed from carbon bisulphide corresponds to a proportion in the paraffin graph. A correction must also be made for the quantity of paraffin estimated from the difference in the specific gravities. As a rule the true percentage of paraffin is equal to the amount found multiplied by the fraction  $\frac{100-x}{100}$ , where  $x$  represents the percentage of carbon bisulphide. Results thus obtained with mixtures rich in carbon bisulphide and paraffin are less accurate than those obtained in the analysis of benzols, but they do not differ materially from the true values.

C. A. M.

**Hydrogenated Chrysalis Oil.** M. Tsujimoto. (*J. Ind. and Eng. Chem.*, 1916, **8**, 802-3.)—Raw chrysalis oil is unsuitable for hydrogenation, but the refined product (*vide* M. Tsujimoto, *J. Chem. Med. Tokyo*, 1914, **17**, 191; *Chem. Rev.*, 1914, 58) can be hardened into a white fat suitable for soap-making by using a nickel catalyst. The fatty acids of chrysalis oil consist of about 25 per cent. saturated and 75 per cent. unsaturated acids (iodine value 178.7). Palmitic but not stearic acids were identified among the saturated acids, and oleic, linolenic and isolinolenic among the unsaturated (Tsujimoto, *J. Soc. Chem. Ind.*, 1908, **27**, 455). The hydrogenated product of the unsaturated fatty acids consists mainly of stearic acid. In addition to palmitic acid, some higher saturated acid or acids are present in chrysalis oil; probably this substance is an eutectic mixture of stearic and palmitic acids. Using the Kreiss and Roth method (*ANALYST*, 1913, **38**, 114) as modified by Normann and Hugel (*ibid.*, 1913, **38**, 432), no saturated acid higher than stearic was found in the hardened oil. An iodine value of the liquid fatty acids exceeding 100 may be expected from a hardened oil having an iodine value above 50, in this respect resembling the fish oils (*vide* Marcusson and Meyerheim, *Zeitsch. angew. Chem.*, 1914, **27**, 201).

H. F. E. H.

**Analysis and Composition of Some Cigarette Papers.** S. Jordan. (*J. Ind. and Eng. Chem.*, 1916, **8**, 812-813.)—The composition of the five samples examined consisted of linen fibre slightly sized with starch or dextrin and filled with the carbonates of magnesium and calcium. The filler in the first three averaged 24 per cent. and the pulp 71½ per cent., while the last two contained 9 per cent. of filler and 86 per cent. pulp. It is possible that a portion of the magnesium was added as the peroxide or oxide for the purpose of accelerating the burning of the paper; nothing injurious was found in the ash, filler, or pulp. The papers burnt to a clean white ash, with an absence of compounds formed by destructive distillation. No alkaloids, alkaloidal salts, or poisonous metals were found. The filler is not materially changed when the paper is burned, and has thus no effect, except to promote combustion and to render the papers impervious.

H. F. E. H.

**Estimation of Dicyanodiamide in Calcium Cyanamide by Caro's Method.** G. Hager and J. Kern. (*Zeitsch. angew. Chem.* 1916, **29**, 308-312.)—Caro's method (ANALYST, 1911, **36**, 76) yields too low results for dicyanodiamide, because a small quantity of this substance is carried down with the precipitate of silver cyanamide even in the presence of an excess of ammonia; another source of loss is due to the fact that dicyanodiamide undergoes slight decomposition, with the evolution of ammonia, when the filtrate from the silver cyanamide is treated with potassium hydroxide and boiled. The loss of dicyanodiamide nitrogen from these two causes increases with the proportion of the substance present in the calcium cyanamide. The authors have made many experiments with a view to preventing this loss, but without success.

W. P. S.

**Analysis of Explosives permitted in America.** C. G. Storm. (*Department of the Interior, U.S.A. Bureau of Mines, Bull. No. 96*, 1916, pp. 1-88.)—The *Bulletin* is published for the purpose of informing manufacturers as to the methods employed in the analysis of explosives in order to determine their permissibility for use in coal-mines. A detailed description is given of the physical and chemical methods (qualitative and quantitative) used for the examination of ammonium nitrate explosives, hydrated explosives, organic nitrate (nitro-starch, etc.) explosives, and nitroglycerine explosives. A few of the methods have a general applicability and are given below; the original should be consulted for the exact details of all the methods.

*Specific Gravity Separation of Ingredients.*—The method depends on the difference in specific gravity of the various components, particularly the mineral salts, and the separations are effected by means of mixtures of chloroform (sp. gr. 1.49) and bromoform (sp. gr. 2.83). For example, the mineral constituents of an explosive, after treatment with ether, contained ammonia, sodium, nitric acid, and chlorine, but it was not possible by the usual tests to say how these were combined. On treating the salt mixture, however, with a chloroform-bromoform mixture of sp. gr. 1.8, crystals of sodium nitrate sank to the bottom and were identified. Sodium chloride, if present, would have been found with the sodium nitrate, but no reaction for chloride was obtained. The lighter portion of the salts gave reactions for ammonia, chloride, and nitric acid, and the mixture therefore consisted of sodium nitrate, ammonium chloride, and ammonium nitrate.

*Estimation of Moisture.*—It is impossible to estimate hygroscopic moisture when salts containing water of crystallisation are present in an explosive. The moisture content may be obtained by difference after all the other constituents have been estimated and the crystallised salts given their full quota of water of crystallisation; but, as some efflorescence may have taken place, it is better to report the difference as moisture *plus* water of crystallisation. An alternative method is to assume average values for the percentages of moisture present in the various ingredients. In the case of nitro explosives, it is found that nitroglycerin does not volatilise to any appreciable extent when dried over sulphuric acid for three days at ordinary pressure; the same is true of crystallised trinitrotoluene and dinitrotoluene, but *o*-mononitrotoluene is appreciably volatile.

*Evaporation of Ethereal Solutions of Nitroglycerin, etc.*—The ethereal solution obtained from a nitroglycerine explosive is best evaporated under a bell-

jar in a current of dry air, the bell-jar being provided with an inlet and outlet. Under these conditions, a low temperature is produced by the evaporation of the ether, and, the air current being dry, there is no deposition of moisture. A weighed quantity of nitroglycerine dissolved in 50 c.c. of ether did not lose more than 1 mgrm. when the ether was evaporated under these conditions. *Estimation of Nitropolyglycerine in Admixture with Nitroglycerine.*—This may be ascertained from the nitrogen content of the mixture; nitroglycerine contains 18.5 per cent. of nitrogen, tetradinitroglycerine 16.19 per cent. The molecular weight of the mixture may also be determined by the boiling-point method, using the Beckmann apparatus and employing pure ethyl acetate as the solvent. An alternative method for identifying nitropolyglycerine in such a mixture depends on the difference in solubility of nitropolyglycerine and nitroglycerine in dilute acetic acid (60 vols. of glacial acetic acid and 40 vols. of water). One gm. of nitroglycerine dissolves in 10.5 c.c. of this dilute acid at 15° C., whilst 120 c.c. of the acid are required to dissolve a mixture containing 82 per cent. of tetranitrodiglycerine. W. P. S.

**Testing the Purity of Turpentine.** A. Krieger. (*Chem. Zeit.*, 1916, **40**, 472-473; through *J. Soc. Chem. Ind.*, 1916, **35**, 746.)—By the following modification of Armstrong's method (*J. Soc. Chem. Ind.*, 1882, **1**, 480), aromatic hydrocarbons and petroleum spirit in turpentine may be rapidly determined with sufficient accuracy for practical purposes. Twenty c.c. of the sample are shaken for ten to fifteen minutes with 100 c.c. of sulphuric acid (80:20; sp. gr. 1.76) in a dry 500 c.c. flask, then diluted with 200 c.c. of water, and distilled with steam until 100 c.c. have passed over. The oily portion of the distillate is measured and treated with 10-15 c.c. of "oleum" (8 per cent. SO<sub>3</sub>), the reaction mixture poured into water, and, if any oil separates, this is recovered by steam distillation and measured; the volume is that of the petroleum spirit present in the sample, and the diminution of volume caused by the treatment with "oleum" corresponds to the content of aromatic hydrocarbons.

## INORGANIC ANALYSIS.

**Potassium Dichromate as an Analytical Standard.** G. Bruhns. (*J. prakt. Chem.*, 1916, **93**, 312-338; through *J. Soc. Chem. Ind.*, 1916, **35**, 908.)—The assertion of Wagner that the dichromates have a stronger oxidising action on hydrogen iodide than chromates, and that thereby the "excess value" of the former compared with sodium chloride or other reliable analytical standard can be explained, was not confirmed. Further, the hypothesis that chromic acid has an activating action on the dissolved oxygen towards hydrogen iodide, and gives lower results if the oxygen is previously expelled from the solution by carbon dioxide, is regarded as quite unjustified, as a diminished value of only 0.012 per cent. was found, a figure which lies within the limits of experimental error. From a series of experiments on the time reaction between very dilute dichromate solutions and hydrogen iodide, the conclusion is drawn that, in order to accelerate the oxidation and prevent a subsequent liberation of iodine, it is preferable to increase the concentration of the acid rather

than that of the iodide. Thus practically correct titrations were obtained after five minutes with dilute dichromate solutions to which only 1 c.c. of  $\frac{N}{2}$  potassium iodide, but 10 c.c. of 9.2 N-sulphuric acid, or 6 N-hydrochloric acid, were added. The use of hydrochloric acid is preferable, as the same quantity of sulphuric acid causes a considerably greater after-liberation of iodine.

**Detection of Nickel in Cobalt Salts. A. R. Middleton and H. L. Miller.** (*J. Amer. Chem. Soc.*, 1916, **38**, 1705-1711.)—The sensitiveness of the dimethylglyoxime test for nickel, especially in presence of large quantities of cobalt, is greatly increased by carrying out the reaction as follows: Alkali cyanide is added to the solution of nickel and cobalt until the precipitate first formed just redissolves. The solution is heated and rotated for five minutes after the change of colour is noted, diluted with water at 85° C. to about 50 c.c., and 1 c.c. of dimethylglyoxime solution added. Silver nitrate solution is then added drop by drop until a permanent precipitate results. When dimethylglyoxime and dilute silver nitrate are thus added to a solution containing alkali salts of nickelocyanide, cobaltcyanide and a small excess only of cyanide, precipitation of silver argenticyanide removes the cyanide ion and promotes decomposition of the nickelocyanide ion, increasing the concentration of the nickelous ion, while the cobaltcyanide ion is precipitated as  $\text{Ag}_3\text{Co}(\text{CN})_6$ , or, if not precipitated, is but slightly decomposed. Comparatively little dimethylglyoxime is then sufficient to precipitate the small amount of nickel present, in part at least. One mgrm. of nickel gives an immediate pink precipitate, whilst 0.02 mgrm. gives a distinct pink precipitate within half an hour, and the sensitiveness is not decreased by the presence of 8,000 times as much cobalt as nickel.

G. C. J.

**Use of Diphenylglyoxime as Indicator in the Volumetric Estimation of Nickel by Frevert's Method. G. L. Kelley and J. B. Conant.** (*J. Ind. and Eng. Chem.*, 1916, **8**, 804-807.)—The steel (1 grm.) is dissolved in 50 c.c. of hot, dilute nitric acid (sp. gr. 1.13), or, if much chromium is present, in 60 c.c. of dilute (1:1) hydrochloric acid, followed, when solution is complete, by nitric acid, drop by drop, until effervescence ceases. To the cooled solution, 12 grms. citric acid, 20 c.c. ammonia (sp. gr. 0.9), and enough of an ammoniacal solution of dimethylglyoxime to precipitate all the nickel, are added, followed by more ammonia to distinct alkaline reaction. After an hour the nickel precipitate is filtered off on an asbestos mat, well washed with water, and then dissolved by passing a mixture of 40 c.c. hydrochloric acid and 10 c.c. nitric acid through the mat, and following this with 100 c.c. of water. The filtrate is evaporated almost to dryness, which destroys the dimethylglyoxime and reduces the concentration of ammonium salts at a later stage, which is desirable. The solution is diluted to 150 c.c., made alkaline by addition of dilute (1:3) ammonia, of which 5 c.c. should suffice, and titrated by the new method. This consists in adding a measured and more than sufficient amount of standard alkali cyanide solution, then diphenylglyoxime as indicator, and finally titrating the excess of cyanide by means of a standard nickel solution. The standard cyanide is added until the opalescence (or bluish tinge) disappears, after which

about 15 c.c. more are added. Five c.c. of the indicator are added, and the titration with nickel solution proceeded with. The indicator is prepared by moistening 1 gm. of diphenylglyoxime with alcohol, dissolving it in 100 c.c. of 5 per cent. sodium hydroxide, and diluting to 1,000 c.c. As an indicator, it is preferable to dimethylglyoxime, because the lower solubility of its nickel complex makes it unnecessary to use it in as high concentrations as is necessary with dimethylglyoxime. Five per cent. of nickel in steel can be estimated with an error not exceeding 0.03 per cent. on the steel. G. C. J.

**Volumetric Estimation of Nitrites. B. S. Davisson.** (*J. Amer. Chem. Soc.*, 1916, **38**, 1683-1687.)—The method described and recommended is a modification of that of Chabier ("Princip. and Pract. of Agric. Analysis," 2nd ed., vol. ii., p. 474). A special conical flask with wide neck is employed. This flask has a small tube fused through the side, and then extending downwards to the bottom of the flask, where it terminates in a horizontal limb, perforated on either side by small holes. Through the large rubber stopper pass a gas outlet, two burettes, and a tap funnel. The neutral or alkaline solution to be tested is introduced into the flask and diluted to about 150 c.c. Potassium iodide (0.5 gm.) and starch solution are added, the stopper inserted and the air displaced by carbon dioxide introduced through the side-tube. The current of carbon dioxide is then moderated and 10 c.c. of 15 per cent. sulphuric acid are added. After a short time the liberated iodine is titrated with thiosulphate. The second burette holds standard nitrite solution in case the end-point with thiosulphate is overstepped. The results with pure nitrite solutions are excellent. Fair results (about 5 per cent. too low) are recorded for solutions containing soil extract rich in organic matter. It is suggested that the influence of organic matter could be corrected by boiling a second sample with acetic acid and making a blank titration, but no experiments on these lines are described. G. C. J.

**Estimation of Silver in Protein Preparations. H. Wastenson.** (*Pharm. Post*, 1916, **49**, 187-188; through *Chem. Zentr.*, 1916, i., 810.)—For the estimation of silver in protein preparations which contain chlorides, from 0.2 to 0.5 gm. of the substance is heated with a mixture of 10 c.c. of concentrated sulphuric acid and 2 c.c. of concentrated nitric acid until nitrous fumes are no longer evolved; the mixture is then cooled, diluted with 25 c.c. of water, heated to expel the water, and then boiled for a further thirty minutes. The clear solution is again cooled, diluted with water to about 100 c.c., and titrated with  $\frac{N}{10}$  ammonium thiocyanate solution in the presence of ferric alum (see also *ANALYST*, 1914, **39**, 279). W. P. S.

**Sodium Pyrogallate as Reagent for Estimation of Oxygen. J. W. Shipley.** (*J. Amer. Chem. Soc.*, 1916, **38**, 1687-1701.)—A number of solutions were prepared containing pyrogallol, sodium hydroxide, and water, in different proportions, several of which proved superior to any solution of potassium pyrogallate as absorbents of oxygen. The most effective solution was prepared by adding 40 c.c. of water to 100 grms. of pyrogallol and adding 100 c.c. of 49 per cent. sodium hydroxide solu-

tion. This solution has five times the absorptive capacity of Anderson's best solution of potassium pyrogallate (*ANALYST*, 1915, **40**, 409), and absorbs oxygen at least as quickly. It is too viscous for use with capillaries of less than 1.5 mm. bore, but solutions containing as little as one-fifth the proportion of pyrogallol above recommended are quite as satisfactory as the best solution of potassium pyrogallate that can be prepared. No carbon monoxide was evolved from any of the series of solutions recommended by the author, but he confirms Lewes's statement (*J. Soc. Chem. Ind.*, 1891, **10**, 407) that carbon monoxide is evolved when gases rich in oxygen are brought into contact with solutions as weak in pyrogallol and alkali as those used by Lewes.

G. C. J.

**Electrolytic Estimation of Silver in Solutions of Silver Chloride in Ammonia.** E. P. Schoch and F. M. Crawford. (*J. Amer. Chem. Soc.*, 1916, **38**, 1682-1683.)—The solution, containing a slight excess of ammonia and about 20 grms. of ammonium chloride, and measuring about 150 c.c., is electrolysed at room temperature with an initial amperage of 0.35, using concentric electrodes of platinum wire gauze about 25 meshes to the cm., with a wire 0.1 mm. in diameter. The total area of the cathode employed is about 90 sq. cm. The electrodes are fixed, but a mechanical agitator is provided. The voltage is kept constant (1.1 between electrodes with the author's apparatus) until the current drops to zero. When the current has fallen almost to zero the voltage is raised to 1.3 or 1.4, and electrolysis continued until a total of twenty-five to thirty minutes has elapsed. This time suffices for 0.5 gm. of silver. Without disturbing the apparatus, about 3 grms. of oxalic acid crystals are added, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus-paper. Without increasing the applied voltage, electrolysis is continued for about twenty minutes. During this stage the last 0.4 per cent. or so of the metal is deposited. The beaker containing the electrolyte is then rapidly replaced by one containing distilled water, and the deposit washed with alcohol and ether and dried high above a Bunsen flame. The deposits are purer than those obtained from cyanide electrolytes.

G. C. J.

**Estimation of Thiosulphate Sulphur in Lime-Sulphur Solutions by Iodine Titration.** P. L. Blumenthal and S. D. Averitt. (*J. Amer. Chem. Soc.*, 1916, **38**, 1701-1704.)—The question of the accuracy of the so-called "iodine methods" for the estimation of thiosulphates and polysulphides in commercial lime-sulphur solutions has been investigated. It is found that an excess of iodine does react with tetrathionate in neutral or faintly acid solutions, upon standing. In every iodine titration on a lime-sulphur solution a small quantity of sulphate is formed; in some lime-sulphur solutions this is the only oxidation product found. The quantity of iodine used to form sulphate in an ordinary titration does not cause an appreciable error in the estimation of thiosulphate. The iodine values obtained after decomposing polysulphides by hydrochloric acid actually represent thiosulphate, since the barium sulphate obtained from such solutions after oxidation agrees very closely with the titration values. The presence of sulphites, which would also be titrated at this point, would tend to cause high results for thiosulphate as calculated from

the iodine value. If anything, the gravimetric results for thiosulphate are a trifle higher than the titration values, which points to an absence of sulphites, although this in itself is not absolute proof of the fact.

G. C. J.

**Estimation of Tungsten by Fieber's Method. Separation of Tin from Tungsten.** E. Dittler and A. von Graffenried. (*Chem. Zeit.*, 1916, **40**, 681-682.) Fieber's method (*ANALYST*, 1912, **37**, 220) was found to be reliable for the estimation of tungsten in ferrotungsten, duplicate results agreeing within 0.1 per cent. In carrying out the estimation the authors recommend that a quantity of the finely powdered substance not exceeding 0.25 gm. be treated with bromine for twenty-four hours, the mixture then treated with 10 c.c. of concentrated hydrochloric acid, evaporated nearly to dryness, and again treated with 3 c.c. of hydrochloric acid and a few c.c. of nitric acid. After two hours the mixture is diluted, the precipitate is collected, washed, ignited at a low temperature, and weighed as  $WO_3$ . This method may also be applied to the analysis of tungsten concentrates containing not more than 10 per cent. of tin, but in this case the traces of tin oxide which remain in the tungstic acid must be removed by volatilisation with ammonium chloride. For the estimation of tin in tin ores containing tungsten 1 gm. of the ore is fused with 8 grms. of sodium peroxide, the melt is dissolved in water and diluted to 500 c.c. After filtration, 250 c.c. of the solution are used for the estimation of the tungsten (by the mercurous nitrate method); a further 200 c.c. of the solution are then treated with 10 grms. of sodium phosphate and acidified. If a slight precipitate forms at this point the mixture is filtered; the precipitate may be silica, or a trace of metastannic acid, and an evaporation with hydrofluoric acid will determine whether silica is present. The solution is now boiled to decompose the peroxide, and, while still boiling, the solution is treated with hydrogen sulphide. The precipitated tin sulphide is collected, washed with dilute ammonium acetate solution, dried, ignited and weighed as  $SnO_2$ , or the tin may be estimated electrolytically.

W. P. S.

**Estimation of Total Hardness (in Waters) by Potassium Palmitate.** M. Tilgner. (*Chem. Zeit.*, 1916, **40**, 675.)—After the temporary hardness of a water has been estimated by titration with hydrochloric acid, Blacher has recommended (*ANALYST*, 1913, **38**, 127) the removal of the residual carbon dioxide by means of a current of air previous to the titration of the total hardness with potassium palmitate solution. As it is difficult to determine when the whole of the carbon dioxide has been expelled, the author prefers to neutralise the dissolved carbon dioxide with  $\frac{N}{10}$  potassium hydroxide solution, using phenolphthaleïn as indicator. The solution is then titrated with potassium palmitate solution as described. It is of advantage to add a little more phenolphthaleïn solution previous to the titration with the palmitate solution.

W. P. S.

## APPARATUS, ETC.

**Comparison of the Relative Efficiency of Laboratory Reflux Condensers.**

**M. V. Dover and J. W. Marden.** (*J. Ind. and Eng. Chem.*, 1916, **8**, 834-836.)—The author has examined a number of condensers, among them being the Liebig, spiral, Allihn, Hopkins, Davies and Friedrichs. H. F. E. H.

**Surface Tension Measurements of Solutions of Soap and Soap-Alkali Mixtures.** **H. G. Elledge and J. J. Isherwood.** (*J. Ind. and Eng. Chem.*, 1916, **8**, 793-794.)—A comparative study has been made of a mixture of soap and various alkalis and alkaline mixtures marketed under trade names, to determine their relative detergent values. H. Jackson (Cantor Lectures, 1907) has shown that the values of the alkaline salts of weak acids—sodium carbonate, trisodium phosphate and borax—are equal when chemically equivalent weights are considered, and that sodium bicarbonate is practically valueless: a fact confirmed by the present authors. The apparatus employed was that described by H. W. Hillyer (*J. Amer. Chem. Soc.*, 1903, **25**, 511, 524, 1256), and consists of a 5 c.c. capacity dropping pipette, with capillary stem terminating with a perfectly plain surface 10 mm. in diameter, upon which the drops form in a bath of kerosene. A 0.4 per cent. solution of soap was investigated in conjunction with a 0.5 per cent. sodium carbonate or other alkalis in equivalent proportions, the drop number being read at a temperature of 100° C. By placing weighed amounts of lamp black on filter papers of uniform textures, treating them with equal volumes of the various solutions of alkali and soap, and weighing the filter papers with the residue of lamp black which was not washed through, it was shown that solutions of the highest drop numbers would, under standard conditions, carry away the greatest amount of lamp black. Water, and the solutions of alkalis used without soap were unable to remove any of the lamp black. It was therefore concluded that solutions giving the highest drop number have the greatest detergent value with respect to unsaponifiable dirt. Alkaline solutions are thus in no sense detergents in the absence of free fatty acids or soaps. Experimental results also show that, within the field examined, the greater the quantity of alkali added to the soap solution the better the detergent properties, the amount of alkali being limited in practice by the harmful effect on fabrics of large concentrations of the hydroxyl ion; such effects being almost negligible in the case of sodium carbonate and cotton up to a 1 per cent. solution of sodium carbonate, provided careful rinsing be employed. This figure is from five to ten times the amount usually employed in power laundries. H. F. E. H.

[*Note by Abstractor.*—No mention is made of the drop-number unit employed, but it would appear to be the actual number of drops counted per unit volume of soap-alkali solution, small drops resulting in a large drop number and *vice versa*.]





## REVIEWS.

A HANDBOOK OF COLLOID CHEMISTRY. By Dr. WOLFGANG OSTWALD. Translated by Dr. MARTIN H. FISCHER. First English edition, from the third German edition. Pp. xii + 278. London: J. and A. Churchill, 1915. Price 12s. 6d. net.

Dr. Wolfgang Ostwald is well known as the energetic editor of the *Zeitschrift für Kolloide*, and as an active worker in the field of "colloidal" chemistry, especially on the literary and organising side. It must be confessed, however, that the present work is disappointing in many respects. There is too much striving after general terms and concepts, and not enough quantitative setting out of facts. The author's tendency to theorise on an insecure basis is well exemplified in the chapter on "The General Energetics of the Dispersoids," where he introduces a mysterious "surface energy of the second order" to account for the phenomena of dispersion. This energetic *deus ex machina* appears more likely to darken counsel than to enlighten our understanding of colloidal phenomena. Extraordinarily little attention is paid to the highly important electrical relations of suspensoid systems. The best part of the book is that dealing with what the author calls the "mechanical properties" of colloid systems. But, taken all round, Dr. Ostwald's work cannot be said to present the reader with a good conspectus of the really salient facts and characteristics of colloid systems. The book lacks both historical sense and due perspective, and, though it contains much interesting matter, it reminds one of the egg of the unfortunate curate. It is essentially not a work to be recommended to those unfamiliar with the subject, though the more advanced worker already versed in colloid matters will probably find many things to interest him.

F. G. DONNAN.

A SENIOR EXPERIMENTAL CHEMISTRY. By A. E. DUNSTAN AND F. B. THOLE. Pp. xiii + 522 and 120 diagrams. London: Methuen and Co., 1916. Price 5s. net.

This comprehensive text-book, which is intended for boys in the upper forms of Secondary Schools and students in Technical Institutes, is divided into two parts. The first of these, containing the theoretical outlines of inorganic chemistry, commences with a concise but adequate historical introduction. The fundamental principles of the science are then developed in logical sequence, taking first the atomic theory and its deficiencies as regards the determination of atomic weight. This difficulty is overcome by the supplementary molecular theory, and the introductory part of the course culminates in the demonstration of the three general methods for ascertaining the atomic weights of elements. The remaining chapters of this section are devoted to the elements of physical chemistry, and deal with osmotic pressure phenomena, electrolytic solutions, ionisation, thermo-chemistry, and the periodic classification of the elements.

Part II. of the treatise contains the descriptive portion of the work, and deals with the elements in their natural families. The chapters on hydrogen and water are followed by a description of the halogens, and this latter section is summarised by a tabulated comparison of the properties of these allied elements. Passing back-

wards along the periodic arrangement, the sixth vertical series is reached, and a chapter is devoted to oxygen and another to sulphur. The relationships of these two elements to selenium and tellurium are exhibited in tabular form. In regular sequence follow nitrogen, phosphorus, arsenic, antimony, and bismuth, and so on through the fourth, third, second, and first vertical series. In taking the periodic classification in this order, series eight is missed at first, but its members are now considered and a chapter on the noble metals is appropriately followed by one on the noble gases.

This method of presenting the principles and facts of inorganic chemistry which makes the subjects follow one another in a logical sequence similar to the regular order of the propositions in Euclidean geometry is in the long run the method most suited for pupils who intend to specialise in chemistry. Two other methods have their adherents. Of these, the heuristic method may be dismissed without further comment as being utterly impracticable except, perhaps, for a class of juvenile Methusalehs who might possibly discover for themselves, more or less imperfectly, a few chemical ideas in the course of a lifetime of 400 years. The remaining method, which has been successfully employed by many teachers of great experience, is to begin with the descriptive chemistry of the commoner materials, using these facts as pegs on which to display an occasional principle. The underlying feature of this method is the idea of putting the concrete before the abstract. The teacher presents a group of facts, and then proceeds to draw certain abstract conclusions. This treatment of the subject is probably more suitable for pupils who, without specialising, are taking a short course in chemistry.

In the present treatise for senior students, Drs. Dunstan and Thole rightly prefer the logical method, and in this respect their practice agrees with that of the reviewer, who has always used this sequence in teaching chemical students. It must, however, be admitted that this mode of presentation leads the student to encounter first the more difficult and transcendental parts of the science, and of chemistry more than of many other studies may it be said with truth, "C'est le premier pas qui coûte."

GILBERT T. MORGAN.

AIDS TO BACTERIOLOGY. By C. G. MOOR, M.A., F.I.C., AND W. PARTRIDGE, F.I.C.

Third edition. London: Baillière, Tindall and Cox. Pp. viii + 278. Price 3s. 6d. net.

The appearance of another edition of this little book indicates that its usefulness is appreciated in a wide circle. In this edition the article on the *Meningococcus* has been very properly much extended, a chapter is devoted to the filterable viruses (an unsatisfactory term), and there are sections discussing the phenomenon of anaphylaxis, the use of vaccines, and soil bacteriology.

The authors state that on the advice of Professor David Ellis they have substituted the classification of Migula for that of Hueppe. This is no great improvement. The use of the name of one of the families only, namely the *Bacteriaceæ*, to supply the name for the whole class at once shows how unsatisfactory this classification is. It would have been better if the authors had had the courage of their

convictions, and had amended the classification in accordance with their criticisms of it. Where so much attention has been given to classification, it is rather surprising that no comment has been made on the use of the terms *treponeme* and *spirochaete*.

The twenty two chapters of the book cover bacteriological theories, apparatus, media and stains, pathogenic bacteria and protozoa, moulds, fermentation, foods and water, and disinfection. A special feature of great value is the inclusion of the results of recent work which has appeared in the journals and in official reports, and which has not yet had time to appear in the larger text-books.

To the analytical chemist the chapters of most interest are those on fermentation, foods, water, soil, and disinfectants. These subjects are very well dealt with, both from the theoretical and practical point of view. In treating of the testing of disinfectants, the description of the Rideal-Walker test from the original paper is given. This is perhaps the briefest description of a new process ever written by its authors, and it is doubtful whether anyone who had not seen the test carried out would be able to do so successfully. This is not of importance, however, as Mr. Partridge has dealt fully with the testing of disinfectants elsewhere.

The book is not meant to be a laboratory manual. It is written as one of a Students' Aids series, and for this it is admirably suited, as well for the medical as for the pure science student. A very large amount of up-to-date information is given in a compact and condensed form. Exception must be taken, however, to the opening paragraph of the book. Here the attempt to describe the position of the bacteria and moulds in the vegetable kingdom is so condensed as to be liable to lead to erroneous deductions on the part of the uninstructed reader. The paragraph should be considerably extended or omitted altogether in a future edition.

There is a very good index.

J. H. JOHNSTON.

**FOOD VALUES: WHAT THEY ARE AND HOW TO CALCULATE THEM.** By MARGARET MCKILLOP, M.A. London: George Routledge and Sons, Ltd., 1916. Price 1s. net.

This little volume ("not a war book," says the author) has been compiled "for the use of those students of diet who wish to undertake quite seriously the consideration of food values and the problems involved in their investigation." Such a work should be of distinct value to that numerous class of well intentioned people who desire to economise without prejudice to proper nutrition, in their daily food expenses, yet lack the data necessary for a successful tackling of the problem.

The view that the "food value" of any particular article of diet is proportional to the price paid for it is probably far too widely held, especially among the very classes vitally concerned in getting value for their money, and it is all to the good that knowledge of the methods and results of impartial investigators, without axes to grind, should be accessible in a popular form such as the present. Unfortunately, the important part played by the psychical factor of food enjoyment as an aid to digestion, is not susceptible of evaluation in calorie units, and so long as human nature remains what it is people will eat, and be willing to pay for, the foods they "fancy," irrespective of the number of protein or fat units obtainable from them.

There still remain, however, many directions in which the information outlined in Miss McKillop's book can be of useful service, and the numerous tables therein, mainly compiled from the works of Dr. Robert Hutchison and Professor Graham Lusk, supplemented by the American Farmers' Bulletins published by the U.S.A. Government, should materially assist the reader in a rational study of nutrition.

HENRY F. E. HULTON.

REATTIVI E REAZIONI. By E. TOGNOLI. Milan: V. Hoepli. Price lire 3.50.

Most English chemists must have been irritated by the frequent references in foreign journals to some little known reaction, without any details of its nature. A little book of this description, in which are given in concise form outlines of a large number of reactions, with the methods of preparing the reagents, will therefore be of the greatest possible help in the laboratory. It includes the general and special reagents used in chemical analysis, tests of purity for the principal reagents, and the preparations of solutions for microscopic and bacteriological work, together with tables of the specific gravities of acids and alkalis. The book is well arranged for ready reference, and is well worth translating into English. C. A. MITCHELL.

ERRATA.

Page 100, line 20, *for* 367 *read* 364.

Page 252, line 21, *for* 47 *read* 469.

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