

# THE ANALYST.

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## OBITUARY.\*

### FREDERICK WALLIS STODDART.

FREDERICK WALLIS STODDART, who died on April 15, 1916, aged fifty-seven, was the son of the late W. W. Stoddart, the first Public Analyst for the City of Bristol, and Public Analyst for the County of Somerset. Frederick Wallis Stoddart was educated at the Bristol Grammar School, at University College, Bristol, and at St. Thomas's Hospital Medical School, where, in 1877, he became assistant to Dr. Bernays, in whose laboratory he worked for three years. On his father's death, in 1880, he succeeded in the Public Analystship of Bristol, which he retained until 1905, and was also appointed Public Analyst for the boroughs of Chard, Salisbury, and Bridgwater. He lectured for many years on the chemistry of public health and on bacteriology in the Bristol Medical School, and made several useful contributions to the literature of the analysis of food, drugs, and water. Most of his papers were read before the Society of Public Analysts and published in the ANALYST, his perhaps most important contribution to that journal being a bacteriological paper, "On the Separation and Identification of the Typhoid and Colon Bacilli." During later years, bacteriological processes occupied a large share of his attention, and he devised a successful mechanical apparatus for facilitating the bacterial oxidation and purification of sewage. He was elected a Fellow of the Society in 1894.

BERNARD DYER.

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

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AN ordinary meeting of the Society was held on Wednesday evening, June 6, in the Chemical Society's Rooms, Burlington House. The President, Mr. G. Embrey, F.I.C., occupied the chair.

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

Certificates of proposal for election to membership in favour of Messrs. C. V. Bacon and K. H. Vakil, B.A., B.Sc., were read for the second time.

Captain N. M. Comber, B.Sc., A.R.C.Sc., was elected a member of the Society.

The following papers were read: "Some Experiences in the Use of Copper

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Sulphate in the Destruction of Algæ," by George Embrey, F.I.C.; "Note on Orange-Pip Oil," by Dorothy G. Hewer, B.Sc.; "A Combined Reichert-Polenske and Modified Shrewsbury-Knapp Process," by G. D. Elsdon, B.Sc., F.I.C.; "The Differentiation between Coconut and Palm-Kernel Oils in Mixtures," by G. D. Elsdon, B.Sc., F.I.C.; "Rapid Estimation of the Strength of Sulphuric Acid," by H. Droop Richmond, F.I.C., and J. E. Merreywether; and a "Note on the Estimation of Theobromine," by Norah Radford (*née* Elliott), B.Sc., and G. Brewer.



### OPIUM-POISONING : DETECTION OF MORPHINE IN ACUTE AND CHRONIC CASES.

By JOHN WEBSTER, F.I.C.

(*Read at the Meeting, May 2, 1917.*)

THE ability of the organism, in the case of "morphia-takers," to decompose morphine to a special degree, and thus to become, to some extent, immune to that drug, is a question of great interest; up to the present, so far as I am aware, it has not been definitely proved.

It has been stated that in cases of death following on chronic morphia-poisoning the analyst is less likely to obtain evidence of the presence of morphine in the organs than in an ordinary case of acute poisoning. This is a question of considerable importance to the toxicologist, as cases may arise of alleged poisoning by morphine in which no definite evidence of the presence of that alkaloid in the various organs of the deceased person has been obtained; yet considerable or even very large quantities of morphine may have been taken not long before death, and have been either directly or indirectly the cause of death.

The two cases which I describe below will demonstrate this:

CASE I.—This was a fatal case of acute poisoning by laudanum. The deceased had taken (as far as could be ascertained) 2 drachms of laudanum (equal to 1·1 grain of morphine) about twenty-four hours before death.

The following organs and fluids were examined: Stomach and contents, portion of small intestine, liver, kidneys, urine. There were also 2 fluid ounces of blood in the jar.

In all the above the presence of morphine was definitely proved, and marked reactions for morphine obtained from the "alkaloidal" residues in every instance.

In the case of the intestines and blood traces only (quite definite, however) were found, too small to be estimated with any degree of accuracy.

From the other organs and fluids the following amounts of morphine were obtained:

Stomach wall	...	...	...	...	1/20 grain
Stomach contents	...	...	...	...	3/30 "
Liver	...	...	...	...	2/10 "
Kidneys	...	...	...	...	1/15 "
Urine	...	...	...	...	1/10 "

CASE II.—In this case the deceased woman had been taking large quantities of laudanum for many years, and was known to have been supplied with 3 ounces daily (=13 grains morphine) for several years. She was supplied, three days before her death, with the usual amount (namely, 3 ounces), and as no laudanum was found on the premises, the presumption is that she had taken it.

The following organs were handed to me and examined for morphine: Stomach (this was empty), liver, kidneys. There was also 1 ounce of blood present in the jar. Unfortunately, I was unable to examine any urine in this case, as the bladder at the time of the post-mortem examination (by Dr. Spilsbury, of St. Mary's Hospital) was quite empty.

In the kidney only was I able to obtain a definite reaction for morphine in the alkaloidal extract. This was too small to estimate, but was definite. In the case of the blood there was a doubtful reaction, but in the liver and stomach the Froehde reaction was quite negative, although fairly large quantities of these organs were operated upon (in the case of the liver 200 grms.).

In both Case I. and Case II. the liver extracts were treated with acetate of lead, and the precipitates examined for meconic acid. It was found present in both the acute and the chronic case.

The morphine in the alkaloidal extracts was estimated colorimetrically by formalin and sulphuric acid (Marquis's reagent; Mai and Rath, *ANALYST*, 1906, **31**, 408).

I am indebted to Dr. Spilsbury for the organs and details in both of the above cases, and I desire also to express my thanks to Col. W. H. Willcox, C.B., C.M.G., in whose laboratory the analyses were made.

#### DISCUSSION.

Mr. E. M. HAWKINS said that in a case of poisoning by morphine tartrate, in which a hypodermic injection of strychnine had been given, he had found the strychnine (although its quantity was very minute), but could obtain no trace of morphine, although it was clearly shown at the inquest that the deceased had had access to morphine tartrate, while the medical evidence was to the effect that death was due to morphine-poisoning. A possible explanation might be that the tartrate, being almost the most soluble of the compounds of morphine, was eliminated very quickly. The urine was not in that case submitted to him. In Allen's "Commercial Organic Analysis" (second edition, vol. iii., part ii., p. 360) reference was made to the difficulty of detecting morphine in some cases, even when it was certain that it was the cause of death.

Dr. A. F. JOSEPH referred to the toxicological detection of opium in cases of poisoning in Ceylon; even when quite large doses of opium had been taken, it was often very difficult or impossible to prove the presence of morphine in the post-mortem productions. He should like to ask whether Mr. Webster had a preference for any particular solvent for the extraction of morphine. The ordinary solvents were troublesome to use, and he was not sure whether the morphine might not form some kind of conjugate complex in the body which might render it even less

soluble than it would be in a pure compound. Apparently toxicological methods for the detection of morphine still required a good deal of study.

Mr. A. CHASTON CHAPMAN remarked that morphine was very readily oxidised, and possibly in the body underwent changes which resulted in its not giving the full morphine reactions, while it might appear in the general alkaloid residue as an oxidised product.

Mr. P. A. E. RICHARDS asked what Mr. Webster considered to be the most sensitive test for morphine.

Mr. WEBSTER, referring to Mr. Chapman's remark, said that the organism undoubtedly was able to decompose morphine, but whether the process was entirely one of oxidation or not he did not know. In fact, so far as he was aware, that point was not definitely proved. Supposing it to be an oxidation process, oxydimorphine being produced, this would be more difficult to detect than morphine itself. Oxydimorphine did not give the ordinary morphine reactions. In the chronic case referred to in the paper, he had obtained from the liver and kidneys alkaloidal residues which gave the general reaction for alkaloids to as great an extent as in the first case. From the whole of one kidney in the second case (*i.e.*, the chronic case), although he was only just able to definitely detect the morphine, there were obtained 6 mgms. of alkaloidal residue in a fairly pure state, giving a strong alkaloid reaction. Possibly the morphine was there mostly in an oxidised form, but the presence of putrefactive alkaloids must be borne in mind. In most cases an appreciable proportion of the morphine would be obtained from the liver. With regard to the quantity that might be taken without fatal result, he had heard on very good authority of a case in which a "morphia-taker" was taking as much as 60 grains of morphine a day. With regard to the statement in Allen's "Commercial Organic Analysis," he did not know to what extent the difficulty might have been due to the methods adopted. Great care was necessary in some particulars. Unless, for instance, the temperature was kept low, the morphine might be destroyed; and the question of acidity was also an important one, so that possibly, in earlier analyses at any rate, failure to find morphine might be due to faults in the methods used. In the two cases now referred to, the analyses were made side by side, and the conditions were as nearly the same as it was possible to have them. For the solvent he preferred a mixture of equal parts of ether and acetic ether. Amyl alcohol was not, according to his experience, so satisfactory as ethyl acetate. Besides being less convenient to work with, amyl alcohol was liable to extract various other bodies to a greater extent than ethyl acetate. He considered the sulphomolybdic acid test to be the best for morphine, but the test with sulphuric acid and formalin was also very satisfactory. With regard to the iodic acid test, the textbooks usually simply stated that on adding iodic acid to a solution containing morphine, with chloroform, and shaking up, iodine was liberated, dissolving in the chloroform with the production of a violet solution. Residues were often obtained which gave that reaction when no morphine was present; but the important part of the test was frequently not mentioned—namely, the addition of ammonia, which, if morphine was present, produced a characteristic brown colour in the aqueous liquid (the colour of the chloroform,

of course, being discharged). The yellow or yellow-brown colour produced on the addition of iodic acid to a solution of a morphine salt is not entirely due to the liberation of iodine.



### SOME MAIN LINES OF ADVANCE IN THE DOMAIN OF MODERN ANALYTICAL CHEMISTRY.\*

A LECTURE DELIVERED BY INVITATION BEFORE THE CHEMICAL SOCIETY ON  
MARCH 15, 1917.

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

ANALYTICAL chemistry has often been referred to as the handmaiden of the other branches of our science, and whilst this was an entirely unobjectionable description in so far as it implied indispensable assistance, it was a little unfortunate in that it carried with it a certain suggestion of inferiority. From the dawn of scientific chemistry in the seventeenth century to a period within the recollection of a good many chemists who are still happily among us, analytical chemistry was almost synonymous with chemistry itself, and it is only in comparatively recent times that it has become a separate branch of applied chemistry, with its own literature, its own aims, and its own specialised practitioners. Whilst the division of chemistry into various separated branches became inevitable with the enormous development of the science, and had its obvious conveniences, the progressive subdivision of work has not been without its drawbacks, and even its dangers. That it has conduced to a narrowness of outlook and to a mental onesidedness is undeniable, and it is becoming increasingly difficult always to maintain a just sense of proportion to view facts in their true perspective and to keep a firm hold on fundamental principles. Of all the various members of the body chemical, perhaps none suffered more at first by this process of subdivision than analytical chemistry. During the first half of the last century chemical analysis occupied a very high position, since not only was it clearly the foundation-stone on which the whole chemical fabric was built, but almost every chemist of distinction practised it assiduously and devoted much of his time to a study of its problems. One need only recall in this connection such names as those of Berzelius, Gay-Lussac, Marignac, Bunsen, Dumas, Stas, Liebig, and Wöhler. With the birth of modern organic chemistry and its colossal development during the past half-century—a development which, be it remembered, was largely dependent in the beginning on the analytical labours of Gay-Lussac, Liebig, Dumas, and other early workers in the field—the analytical branch of our science was gradually relegated to a comparatively humble position. In the presence of this new and fertile field, in which every thrust of the spade served to bring to light some discovery of the highest importance and of the most absorbing interest, it is scarcely to be wondered at that the great majority of chemists should have forsaken the older branch, and that the

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all-important foundation-stone should have tended to become regarded more and more as merely the useful handmaiden. That the lamp of analytical chemistry was kept well alight during the period in question, notwithstanding the superior attractions of organic chemistry, is evidenced by the epoch-making researches of Bunsen and Kirchhoff on spectrum analysis, by numerous records of observations on the qualitative electrolytic decomposition of metallic salts, on which the important branch of electrochemical analysis was later on to be founded, chiefly by the labours of Classen and his students, and by the many investigations having for their object the perfection and simplification of methods of gas analysis. Last, but not least, I may mention in this connection the establishment of the Fresenius Laboratory in Wiesbaden in 1848, and a few years later (1862) the foundation of the *Zeitschrift für analytische Chemie*, the first journal, I believe, which was devoted exclusively to the interests of analytical chemistry. Our own Journal, THE ANALYST, did not appear until 1877.

Great as is the temptation, it is not my intention to deal at any length with the history of analytical chemistry during the latter half of the nineteenth century. I will merely content myself with remarking that at a certain point in that history the rate of progress in its scientific development had slowed down so considerably that any chemist taking a superficial survey might well have been justified in supposing that future advances would be restricted to improvements in existing methods and to the extended application of those methods to the solution of new technical and industrial problems. That new lines of progress would be opened up must have seemed highly improbable, and it is recorded that a certain distinguished German chemist went so far as to utter the dictum that analytical chemistry presented no further problems. My task this evening will be to indicate briefly a few of the main lines along which the scientific development of modern analytical chemistry has proceeded, and to deal—however inadequately—with what I conceive to be the main causes of its restoration to something of its old position as a living and progressive part of our science. Foremost among these causes has unquestionably been the almost unparalleled growth during comparatively recent years of that younger member of the chemical family—I mean physical chemistry. That a proper understanding of analytical chemistry, as of every other department of the science, is dependent on a knowledge of those fundamental laws which it is the special province of physical chemistry to elucidate will appear to most chemists of to-day a self-evident proposition. Yet it was not until the publication of Ostwald's "Wissenschaftlichen Grundlagen der analytischen Chemie" in 1894 that this all-important truth was presented to the chemical world, and not until some years later that it received anything like general recognition—at least in this country. To many generations of students chemical analysis had been taught as a useful art, consisting largely of a series of recipes which, if followed conscientiously, would usually lead to the desired result. Those recipes had often the authority of great names behind them, and so far as they went were admirable; but how many of those students were taught anything of the underlying principles, or were put by their teachers in a position to make for themselves such modifications of the orthodox processes as might at times become necessary? The

result was to manufacture a body of more or less mechanical handworkers, and if, as fortunately happened, a number of these showed initiative and developed originality, it was in spite of, rather than in virtue of, the instruction they had received. This state of affairs was, however, inevitable, since, as Ostwald has pointed out, it was only with the advent of the general theory of chemical reactions and states of equilibrium that it became possible to elaborate a theory of analytical reactions and to place analytical chemistry on a really scientific foundation. It was then the beneficent work of physical chemistry to infuse new life into analytical chemistry, to help to place it on a firm and wide basis, and to do much to remove the reproach that this branch of chemical science, whilst representing a useful field of highly skilled manual labour, could scarcely be regarded as an intellectual occupation.

In three main directions this revivifying influence has made itself felt during the past twenty years. In the first place, it has supplied the explanation of a vast number of facts which had been arrived at empirically, and are of the greatest importance to the analyst; in the second place, it has greatly stimulated and directed original research, and, finally, it has enriched analytical chemistry with a number of new appliances, and has resulted in the introduction of many new methods of inquiry.

Of all the theories of modern physical chemistry, none has had so far-reaching and important an effect on the development of analytical chemistry as those connected with the nature of solution. It is not, in fact, going too far to say that the general adoption of these theories and their application to analytical processes was the means of placing analytical chemistry for the first time on a really scientific basis. The years 1885, 1886, and 1887, which for chemists will ever be memorable for the publication of the great generalisations of van't Hoff and Arrhenius, may justly be regarded as dates of outstanding importance in the history of analytical chemistry. To deal with this aspect of the subject at any length before an audience of chemists is quite unnecessary. That the theory of electrolytic dissociation has not met with universal acceptance is of little importance from this point of view, for I believe that even those chemists who regard it with the greatest disfavour would be inclined to admit that no other theory is able to explain so much or is capable of welding the whole chaotic mass of analytical phenomena into such a coherent and harmonious whole.

The manner in which it has contributed to the building of a serviceable, if not complete, theory of indicators, and its helpfulness in explaining the phenomena of electrolysis, hydrolytic dissociation, and mass action, are too well known to need more than a passing reference.

As a further instance of the fruitfulness of this concept and of its value to analytical chemistry I may mention the application of the conductivity method to the determination of the point of neutrality of liquids. This method, first suggested by Küster and Grütters in 1903, has since received a considerable amount of attention at the hands of a great many workers, and the numerous contributions to the subject by Sørensen, Michaelis, and others, represent a storehouse of very valuable information in connection with the applicability of certain indicators to

special purposes, the preparation of solutions of standard reaction, and the electrometric measurement of hydrogen-ion concentration. This work, which is undoubtedly capable of further development, has already proved of very great value in the investigation of certain biochemical problems, and will, no doubt, find extended application in the wider field of technical analysis.

In further exemplification of the close and fruitful connection between physical chemistry and analytical chemistry, I may just refer to the vast amount of work which has been done during comparatively recent years in connection with the colloidal state of matter and in the study of catalytic phenomena.

As showing moreover, how some of the more recondite physical properties of matter may prove to be of practical importance to the analyst, I may perhaps be permitted to refer to the papers which I have published, alone or in collaboration with H. D. Law, on the reducing action of hydrogen in its relation to analytical processes. In those papers it has been shown that much depends on the nature of the metallic surface from which the hydrogen is evolved. Thus, certain specimens of zinc which, owing to the presence of small quantities of impurities, are useless for the purpose of detecting and estimating minute traces of arsenic by the modified Marsh-Berzelius method, can usually be made suitable by coating the zinc with pure cadmium, thus producing a surface from which the hydrogen is evolved in a state of higher chemical activity.

In the same way, when an electrolytic method of estimating traces of arsenic employed, much greater sensitiveness is obtained by using a lead or a cadmium rather than a platinum cathode. It is, of course, tolerably certain that the reducing efficiency of hydrogen, whether obtained by the interaction of metal and acid or by an electrolytic process, is dependent upon a number of factors, partly chemical and partly physical, and that the reactions are, in point of fact, very complex. There can, however, be very little doubt that among these factors the question of "potential" or "overvoltage" plays a prominent and important part.

The effect of employing cathodes of different metals in the reduction of arsenious oxide is shown by the following results:

Cathode.	Arsenious Oxide added.	Arsenious Oxide found.	Arsenious Oxide left in Flask.
Lead ... ..	10	10	—
Cadmium ... ..	10	10	—
Tin ... ..	10	10	—
Copper ... ..	100	10	90
Silver ... ..	50	10	40
Nickel ... ..	40	20	20
Platinum (black) ... ..	1,000	0	1,000
Iron ... ..	50	5	45

From this it will be seen that even the overvoltage of metals—a subject which at first sight might appear to be mainly of academic interest—has, in fact, a very direct and important bearing on some of the everyday operations of the analytical laboratory.

Time forbids that I should deal at any greater length with this side of the



intimate relationship existing between these two branches of our science, and I will now refer briefly to the service rendered by physical chemistry in the direction of increasing the analyst's equipment and of multiplying his means of attack.

To the balance, the microscope, and the spectroscope, there have been added from time to time a number of other physical instruments, some of which have revolutionised many of the older branches of analytical chemistry, and have even been the means of giving birth to new ones. Whilst in its cruder forms the polariscope goes back to the beginning of the last century, or even beyond, the modern polarimeter is of comparatively recent birth, and since the introduction of the Jellet instrument about 1860, the labours of physicists and opticians have been almost continuously devoted to the perfecting of this highly important analytical appliance. Without it, carbohydrate analysis would to-day have been in a very different position, and many of the problems which confront the analyst in connection with the sugar, starch, confectionery, essential oil, and brewing industries would have been impossible of solution. In addition to these main applications of the polarimeter, there are many others of less importance, and new ones without doubt remain to be discovered.

Next, perhaps, in importance comes the refractometer, an instrument which finds wide and ever-increasing application in the analytical laboratory. What the polarimeter is to carbohydrate analysis the refractometer is to the analysis of fats and oils, and its assistance has been successfully invoked in the examination of brewing materials, milk serum, sugars, methyl and ethyl alcohols, glycerol, and many other natural and artificial products.

The calorimeter in all its forms and with all its modern refinements, as well as the various mercurial, resistance, and thermo-electric heat-measuring instruments, represent another section of what, for want of a better term, may be called analytical procedure, for the development of which the chemist is chiefly indebted to the physicist.

In addition to these physical instruments of almost everyday use, passing reference may be made to modern spectrographic apparatus, appliances for the determination of electrical conductivity, instruments for the measurement of colour and of turbidity, and, lastly—and of most recent introduction—apparatus suitable for making estimations of radioactivity.

I think I have said enough to show the general nature of the relationship existing between physical and analytical chemistry, and to indicate one of the main lines along which the latter branch of our science has advanced during comparatively recent years. Such, indeed, is the intimacy of the connection that, as new discoveries are made by physical chemists, they will almost inevitably be utilised in the consolidation or extension of that great field of analytical chemistry in which so many of us are proud to labour.

I will now turn for a brief space to another side of my subject. If organic chemistry, by its rapid growth, vast importance, and all-compelling interest, was responsible for the temporary neglect of analytical chemistry at one stage of its history, it has since made ample amends by furnishing the analytical armoury with a number of very important weapons. If it has presented to the analyst innumer-

able problems of the highest importance, it has also supplied in many cases the means for their solution. To speak more plainly, it has been found during recent years that many of the more or less complex products of the organic laboratory are, in fact, very valuable analytical reagents, and that by their use old problems may often be better solved and new ones successfully attacked.

One of the earliest of these was phenylhydrazine, by the discovery of which in 1878 E. Fischer placed in the hands of chemists a reagent which is now almost as necessary in the analytical as in the purely organic laboratory. In qualitative analysis, it is only necessary to refer to the application of the osazone reaction to the identification of the various sugars, a problem the difficulty of which is only equalled by its importance, whilst in quantitative analysis it has a large sphere of usefulness in the estimation of aldehydes and in the quantitative examination of compounds containing the carbonyl, nitroso-, and nitro-groups. In addition to phenylhydrazine itself, considerable use has been found for some of its substituted derivatives, such as *s*-phenylmethylhydrazine, *s*-diphenylhydrazine, and the *p*-bromo- and *p*-nitro-compounds. In this connection, reference may also be made to  $\beta$ -naphthylhydrazine, a substance which Ekenstein and Lobry de Bruyn have shown to be of great service in the recognition and separation of certain carbohydrates and for the estimation of vanillin, and to semicarbazide, a substance which has proved so useful in the isolation and identification of the aldehydic and ketonic constituents of many essential oils.

As further examples of organic compounds which have been successfully applied to the identification and estimation of organic substances of technical importance, mention may be made of phloroglucinol, digitonin, picric acid, and picrolonic acid. The estimation of pentoses and pentosans in certain foodstuffs and in many agricultural products is often a matter of importance, and, as is well known, the method almost invariably adopted consists in distilling the substance under investigation with hydrochloric acid and estimating the furfural in the distillate. For this purpose, phloroglucinol, which forms with furfural a sparingly soluble compound—the so-called phloroglucide—is often made use of. In the same way, methyl-pentoses and methyl-pentosans can be estimated as the corresponding phloroglucinol compound. Further than this, the difference in the solubility in alcohol of the two phloroglucides affords a means for the approximate separation of the pentoses (for example, arabinose and xylose) and the methylpentoses (for example, rhamnose and fucose).

In 1910 Windaus made the discovery that one molecule of cholesterol is capable of uniting with one molecule of digitonin to form a compound of high molecular weight ( $C_{82}H_{140}O_{29}$ ) which is very insoluble, and can consequently be conveniently employed for the estimation of the former substance—a matter of considerable importance to physiological and occasionally to technical chemists. Since digitonin also forms a similarly insoluble compound with phytosterol, it has been employed for the purpose of obtaining either or both of these alcohols in a pure condition prior to converting them into their acetates, as in the ordinary Bömer test. In this way the detection of vegetable oils in oils of animal origin, or *vice versa*, is much facilitated.

The extensive use made of picric acid for the identification, and occasionally for the estimation, of alkaloids and other bases is too well known to need more than a passing reference, and more recently picrolonic acid (dinitrophenylmethylpyrazolone) has been employed for the same purpose. The picrolonates are in some cases less readily soluble than the corresponding picrates, crystallise well, and are often very characteristic. The importance of adding to our means of identifying such substances as arginine, histidine, lysine, guanidine, and other physiologically important bases, will be obvious to all who have followed the developments of modern biochemistry.

It will be seen that the instances I have given above are all cases in which one organic compound has been made use of for the identification or estimation of another. I will now refer to a more interesting and, in a sense, more significant application of certain organic compounds—namely, to the detection and estimation of what may be conveniently described as the simpler inorganic acids and bases.

One of the earliest of these is the *m*-phenylenediamine test for nitrous acid, for which we are indebted to Peter Griess. Already in 1870 Griess had recommended the use of one of the diaminobenzoic acids for the detection of nitrous acid, and in 1878 he proposed the use of the above reagent as being much more sensitive, and the method was worked out on the quantitative side about the same time by Preusse and Tiemann. In the following year Griess published a further paper, in which he recommended for the same purpose the use of a mixture of sulphanilic acid and *α*-naphthylamine—a method which is occasionally ascribed to Ilsvay, who merely recommended the substitution of acetic acid for a mineral acid as the acidifying medium.

Another well-known colorimetric method for the detection and estimation of minute quantities of nitrous and nitric acids is due to Lunge, and involves the employment of diphenylamine. Although, unfortunately, not specific, it has proved of the greatest service in the estimation of minute traces of nitrogen acids in sulphuric acid, milk, and other technical products.

A good many other organic compounds, such as phenolsulphonic acid and resorcinol, have been recommended at various times for the detection and estimation of nitrates and nitrites, but it will not be necessary to refer to these in any detail. It will, of course, be readily understood that the nature of my subject—even if time permitted—renders it unnecessary for me to deal by way of illustration with more than a few of the instances in which organic compounds have been pressed into the service of this branch of general analytical chemistry, and I shall confine my attention to those methods which have been very thoroughly tested and have been elevated to the rank of standard processes.

Whilst dealing with the estimation of commonly occurring inorganic acids, mention may be made of the benzidine method for sulphuric acid and the use of "nitron" for the estimation of nitric acid. The former method, which owes its origin to W. Müller, depends on the fact that benzidine sulphate is almost entirely insoluble in cold water in the presence of an excess of benzidine hydrochloride, and since the method is a volumetric one, it possesses the advantage of rapidity.

Notwithstanding that it has been studied and recommended for special pur-

poses by such experienced workers as Raschig and G. v. Knorre, it is obviously very unlikely that any organic compound will ever replace barium as a general reagent for the estimation of sulphuric acid. I have referred to this method rather in the hope that it may stimulate investigation in this direction, since the occurrence of an insoluble sulphate of an organic base, and still more the discovery of an insoluble nitrate, such as is referred to below, render it probable that similar insoluble salts, suitable for analytical purposes and possibly representing some well-defined advantages over existing methods, still remain to be discovered.

In 1905, in the course of an investigation of the *endo*-imino-triazoles, Busch observed that these bases are characterised by the formation of very sparingly soluble nitrates. By a fortunate chance, it happened that the most readily prepared of these compounds—namely, 1:4-diphenyl-3:5-*endo*-anilo-4:5-dihydro-1:2:4-triazole—was the one which gave a nitrate possessing the highest degree of insolubility. One molecule of this base unites with one molecule of nitric acid, giving a compound of the formula  $C_{20}H_{16}N_4 \cdot HNO_3$ , and it is capable of giving a precipitate in a solution containing as little as 1 part of nitric acid in 80,000 parts of water.

This base, which can be obtained commercially under the more easily remembered and more euphonious name "nitron," is very easily employed as a reagent, and furnishes us for the first time with a means of making a direct gravimetric estimation of nitric acid. It has been applied with success to the estimation of nitrates in water and in a considerable number of commercial products, such as natural nitrates, nitrocellulose, soils and plants, and is particularly well suited for the estimation of nitrates in liquids containing much organic matter. It has also been found that the method is applicable to the estimation of picric acid, since 1 part in 250,000 parts of water gives a precipitate of "nitron" picrate. The discovery of unexpectedly useful properties, such as the insolubility of this nitrate—and many other striking examples might easily be quoted—adds a great attraction to the study of pure, synthetic organic chemistry.

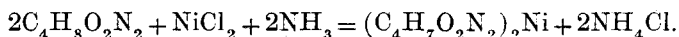
I will now pass for a few moments to the application of organic compounds to the quantitative separation and estimation of many of the commoner and some of the rarer metals.

One of the first substances to be used for this purpose, and one which is susceptible of somewhat wide application, is nitroso- $\beta$ -naphthol, which has been very thoroughly studied by G. v. Knorre and his colleagues. It has been found, for example, that by the use of this reagent nickel may be separated from cobalt; iron from aluminium; copper from cadmium, magnesium, manganese, zinc, mercury, and lead; iron from manganese, zinc, nickel, and chromium; iron from glucinum; copper, iron, and cobalt from antimony and arsenic; and iron from zirconium.

Many of these separations can be effected with ease and with accuracy, the metallic derivatives of the nitroso- $\beta$ -naphthol being easily dealt with, and being, of course, readily converted by ignition into the corresponding oxides. The copper compound has the formula  $(NO \cdot C_{10}H_6 \cdot O)_2Cu$ .

*m*-Nitrobenzoic acid has been successfully used for the quantitative separation of thorium from cerium, lanthanum, and didymium in the analysis, for example, of monazite sands, whilst palladium can be readily separated from platinum and other metals of the platinum group by means of acetylene.

*De minimis non curat* may be true of the law, but it certainly is not true of modern chemistry, which in certain directions is almost coming to be regarded as the chemistry of traces. The importance to the physiological chemist, to the metallurgical chemist, and to the food chemist, of being able to detect with certainty small traces of substances is well recognised, and peculiar interest therefore attached to Tschugaev's observation in 1905 that dimethylglyoxime constitutes a delicate test for nickel. He showed, in fact, that it was capable of detecting 1 part of the metal in more than 1,000,000 parts of water, and of affording certain indications, even when cobalt was present to the extent of 5,000 times that of the nickel. The reaction may be represented by the following equation:



This method has been very thoroughly investigated by many chemists, some of whom have introduced modifications with the object of increasing its sensitiveness. Thus, it has been quite recently stated that, by the adoption of certain modifications, as little as 0.02 mgrm. can be readily detected in 50 c.c. of solution, whilst some years ago Armit and Harden stated that they were able, when working with pure nickel sulphate, to detect as little as 0.001 mgrm. in 30 c.c., whilst 0.003 mgrm. gave a very marked pink colour in that volume of liquid.

As a reagent for the colorimetric estimation of traces of nickel, dimethylglyoxime possesses very great and obvious advantages over the ammonium sulphide method. The coloration is more characteristic, traces of iron do not interfere, and the method is, of course, much more sensitive.

As a means of estimating nickel in alloys, particularly in the presence of cobalt, zinc, and iron, this method has proved exceedingly useful, being rapid and possessed of a tolerably high degree of accuracy.

Another oxime, namely, *a*-benzildioxime, originally described by Tschugaev, has been recommended by Atack for the qualitative detection of nickel and for its estimation. It forms an intensely red nickel compound having the formula  $C_{28}H_{22}O_4N_4Ni$ , containing only 10.9 per cent. of nickel. It is even more sensitive than dimethylglyoxime, and it has been stated that with this reagent 1 part of nickel in 10 million parts of water can be detected. Like dimethylglyoxime, it has been recently utilised for the detection of traces of nickel in hardened edible fats, in which nickel has been used as a catalyst. When working on 50 grms. of the fat, 1 part of nickel in 5 million parts of the fat can be detected. It is of interest to note, in passing, that the  $\beta$ -isomeride does not yield the nickel reaction.

Another organic compound utilised during recent years for the estimation of nickel is dicyanodiamidine. This reagent, which was originally recommended by Grossmann in 1906, is used in the form of the sulphate, and the nickel compound, which is a well-crystalline, yellow substance, has the composition  $Ni(C_2H_5ON_4)_2 \cdot 2H_2O$ . By the use of this reagent nickel may be separated from cobalt, iron, chromium, zinc, and other metals, and, given suitable conditions, may be estimated with a high degree of accuracy. It has, in fact, been used very largely, particularly in Continental laboratories, for the analysis of German silver, commercial nickel, nickel steel, and other alloys. Although it is not by any means

as sensitive as either of the two above-mentioned reagents, it is said to be capable of detecting 0.5 mgrm. of nickel in the presence of as much as 1 grm. of cobalt.

The above methods for the estimation of nickel are of great technical importance, since the precipitates are crystalline and form readily at the ordinary temperature. They can be filtered with ease, they are of constant composition, and the percentages of nickel are not high. The employment of these more or less complicated organic reagents is, as I have indicated, of comparatively recent introduction, and it is not too much to hope that similarly serviceable methods will be discovered for the separation and for the rapid and accurate estimation of other closely allied elements.

In 1909 Baudisch discovered that the ammonium salt of nitrosophenylhydroxylamine ( $C_6H_5 \cdot N[NO] \cdot ONH_4$ ) was capable of being used for the quantitative precipitation of iron and of copper, and for the separation of these metals from a number of others with which they are frequently associated in practice. This substance, to which the simpler name "cupferron" has been applied, has been found to be capable of somewhat wide application, and has proved a valuable addition to our laboratory reagents.

Ferric iron is precipitated completely in cold solutions containing hydrochloric, sulphuric, or acetic acids as the compound ( $C_6H_5 \cdot N[NO] \cdot O$ )<sub>3</sub>Fe, and may readily be separated from aluminium, chromium, and, indeed, from most other of the common metals, including, by a special process, even copper.

The method has proved useful for the separation and estimation of iron in a number of commercial products, and R. Fresenius, who has submitted it to a critical study, states that the separation of iron and aluminium can be carried out more conveniently and with greater accuracy by the use of this substance than by any other gravimetric method.

I do not propose to enter into any details of the various separations effected by this reagent, but will confine myself to pointing out that by its aid copper may easily be separated from cadmium, zinc, and many other metals, and that both titanium and zirconium may be separated from iron and from aluminium. The titanium compound is a bright yellow substance having the formula ( $C_6H_5 \cdot N[NO] \cdot O$ )<sub>4</sub>Ti.

As an example of the degree of accuracy which may be reached in these separations, it may be pointed out that, when quantities of iron varying from 0.03 grm. to 0.3 grm. were precipitated in the presence of quantities of aluminium and chromium equal to fifty times the weight of iron present, the error rarely exceeded  $\pm 0.2$  mgrm. I mention this detail merely for the purpose of showing that in the case of these complex organic reagents, the many advantages which are frequently obtained are not necessarily secured at the expense of accuracy.

I think I have dealt at sufficient length with this division of my subject, and I will now turn for a few moments to the consideration of a third main line of advance—namely, that concerned with the utilisation of what may be conveniently called biological methods. In the future we may succeed in synthesising enzymes and even precipitins, but that day is not yet, and for some time to come we must remain dependent on the activity of the living organism for the reagents to which I am now referring.

With the mechanism of enzyme action we are not now concerned. What is of importance from the analytical point of view is its specific character. To such an extent is this the case that the enzymes are actually capable of discriminating between certain of the carbohydrates and their optical isomerides. Thus, *d*-glucose, *d*-mannose, *d*-fructose, and *d*-galactose, are fermentable by yeast, whilst their optical isomerides are unfermentable.

In order that a given sugar other than the four above mentioned may be fermented, it is essential that the yeast employed should contain the enzyme necessary for its conversion into one or other of those hexoses. Now, yeasts of different species do not all contain the same enzymes, and it happens, therefore, that a certain species of yeast may be capable of fermenting one carbohydrate and incapable of fermenting another.

Of the various enzymes, invertase is one of the most widely distributed among the saccharomycetes, and consequently the great majority of yeasts are capable of fermenting sucrose. On the other hand, lactase occurs in only a comparatively small number of species, and consequently a great many yeasts, including the ordinary brewers' yeast, are incapable of fermenting lactose.

The following table may be of interest as showing at a glance the behaviour of certain of the yeast species towards several of the more commonly occurring sugars:

Yeast.	Dex- trose.	Fruc- tose.	Man- nose.	Galac- tose.	Malt- ose.	Su- crose.	Lac- tose.
<i>Sacch. cerevisiæ</i> ...	+	+	+	+	+	+	0
<i>Sacch. cerevisiæ</i> , Carlsberg	+	+	+	+	+	+	0
<i>Sacch. Pastorianus</i> ...	+	+	+	+	+	+	0
<i>Sacch. ellipsoideus</i> ...	+	+	+	+	+	+	0
<i>Sacch. Marxianus</i> ...	+	+	+	+	0	+	0
<i>Sacch. exiguus</i> ...	+	+	0	+	0	+	0
<i>Sacch. Ludwigii</i> ...	+	+	+	0	0	+	0
<i>Sacch. anomalus</i> ...	+	+	+	0	0	+	0
<i>Sacch. fragilis</i> ...	+	+	+	+	0	+	+
Kefir ...	+	+	+	0	0	+	+

The sign + indicates that the yeast in question is capable, and the sign 0 that it is incapable, of bringing about fermentation.

The secretion of any particular enzyme appears to be a very constant attribute of a given species, and it has not been found possible by varying the nature of the food-supply or the general environment of a given species to cause it to secrete other enzymes than those normally present. It is this constancy of enzyme production and this selective character that render certain of the yeast species so useful to the analyst, enabling him to arrive at the composition of complex carbohydrate mixtures, the analysis of which would be impossible by any other means.

The method is clearly one which must be applied with caution, and it demands, moreover, some biological training on the part of the operator. The technique, however, is not difficult, and at the present day the majority of analytical chemists, particularly those who are concerned with the analysis of foodstuffs, realise that a certain amount of training in elementary bacteriology is a necessary part of their professional equipment.

It will, of course, be clear that, in addition to yeasts, other organisms which secrete enzymes, such as moulds, may be utilised for analytical purposes, and the preparation of Taka-diastrase from *Aspergillus oryzae* is an illustration in point. *Torulæ*, again, have recently been pressed into the service, since some of these, unlike the yeasts, do not contain any invertase, and so are capable of fermenting away dextrose and fructose, leaving sucrose unattacked. Biological methods such as I am now referring to are in everyday use in the analysis of many sugar products, such as commercial glucoses and invert-sugars, and find extensive employment in the analytical examination of complex carbohydrate mixtures such as many of the prepared foods intended for infants and for invalids.

As one further example of the usefulness of this method, it may be pointed out that, whilst the top yeast as obtained in English breweries converts raffinose into fructose and melibiose, the bottom yeast as obtained in Continental breweries, which contains melibiase as well as invertase, converts it into fructose, galactose, and dextrose—that is to say, into completely fermentable products. It is therefore possible by employing these two types of yeast, and by making a simple polarimetric observation, to estimate the amount of raffinose present in a mixture of sugars—a problem which only a few years ago would have been considered impossible of solution.

Another “analytical” method of a more definitely biological character, but one which has already shown itself to be of great practical importance, is that depending on the “precipitin” reaction—a reaction which permits of the identification of so-called homologous proteins and their differentiation from others which they resemble so closely that they are indistinguishable by purely chemical means. The principle underlying the method is that if a solution of any given protein be injected into the blood of an animal, the blood-serum of that animal will produce a precipitate with an infusion containing the particular protein injected, but not with any other. Thus, if horse-blood serum be injected into a rabbit, the serum of the rabbit’s blood will produce a precipitate when added to an extract of horseflesh, but not with an extract of any other kind of flesh. It thus becomes possible by means of this method to identify horseflesh in mixed foodstuffs, such as sausages. It is also possible to detect small quantities of castor seeds in feeding cakes, to distinguish between hen-egg albumin and the albumin of the eggs of other birds, between the milk of one animal and that of another, between genuine and artificial honey, and even, so it is stated, between the seeds of two-rowed and of six-rowed barley. The importance of the reaction for the identification of human blood in medico-legal investigations is well recognised.

I have now touched on a few of the main lines along which analytical chemistry has advanced during recent years, and have endeavoured to show that, so far from being the exhausted and lethargic handmaiden, it is, in fact, as alive, as progressive, and as originative of research, as any other branch of our science. That this is not always fully realised, and that there has been—and is even now in some quarters—a tendency to regard analytical chemistry merely as a useful art and its practitioners as highly skilled labourers, is unhappily the case. That there are



here and there a few analysts to whom that description might be correctly applied is undoubtedly true, but the same is, of course, equally true of the medical and other professions.

The analytical chemist of to-day is, in fact, being continually faced with new problems that frequently demand for their solution the possession in a high degree of those special qualities of intellect and character which go to make the successful investigator in the domain of pure chemical science. For many chemical consultants life is a continuous series of technical problems, and I am not indulging in any exaggerated language when I say that the really successful consulting and analytical chemist must not only have a good general scientific training, an extensive knowledge of general chemistry, and a genuine love of his work, but he must be mentally alert and adaptable and possess the aptitude for research in a high degree.

With regard to the teaching of analytical chemistry, there is much that I should like to say if time permitted, and in particular I should like to plead again for the establishment in our universities and university colleges of chairs of analytical chemistry. I have already dealt with this subject at some length in an address to another society, and perhaps I may be allowed, in concluding, to quote the following remarks from that address:

“Having very briefly touched on the nature and extent of the scientific equipment needed for the successful practice of analytical chemistry, we may reasonably inquire whether the training which our young professional chemists obtain is such as is calculated to insure the best results. Whilst there may possibly be some difference of opinion as to the precise position which a study of chemical analysis should take in the training of the chemical teacher, there can surely be none as to its supreme importance in the training of the professional chemist. In the great majority of cases it is the actual instrument by which, directly or indirectly, he is to earn his livelihood, and in every case it must tend to produce (if properly taught as a living subject and not as a mass of tedious prescriptions and formulas) a deeper insight into the nature of chemical reactions, an appreciation of the influence of mass and other disturbing factors, and a recognition of the importance of attention to minute detail. In addition to this, it affords endless opportunity for the acquirement of dexterity in constructing and manipulating scientific appliances, and in all these ways renders invaluable service in the making of the successful technical chemist. Now, if all this be true—and I do not see how it can be denied—analytical chemistry ought clearly to take an outstanding position in our universities and university colleges, as it is from them that, more often than not, the young chemist proceeds directly to the practice of his profession. Unfortunately, the position which it takes in those institutions is not, as a rule, a high one, nor one at all commensurate with its importance. I believe I am correct in saying that in no university in this country does a chair of analytical chemistry exist, and that a subject which is admittedly of such great importance is entrusted to teachers who, however well qualified and capable they may be, have, as a rule, to teach it, if I may use the expression, incidentally. . . .

“So large a subject, and one which is in constant process of development,

might well, it seems to me, be entrusted to a specially appointed professor, who would have the opportunity of keeping himself fully abreast of the developments of his subject, and who would have the time to deal with it in a manner practically impossible under the existing conditions. Such chairs of analytical chemistry exist in very many of the more important American and Continental universities, and it can scarcely be contended that what has been found desirable in so many other parts of the civilised world is unnecessary in Great Britain. Chairs of analytical chemistry, for example, exist in Yale, Virginia, Johns Hopkins, Cornell, and Columbia Universities, to name only those of which I know, and I believe I am correct in saying that in Columbia University there are no fewer than three such professors. In many of the university prospectuses great emphasis is laid on the importance of analytical chemistry, and from one of the Yale calendars I cannot refrain from quoting the following words: 'There is probably no branch of chemical study as important as qualitative analysis in its use in developing the reasoning faculties and enabling the student to generalise and to classify chemical phenomena.' In Heidelberg, Munich, Leipzig, Würzburg, and other German universities, in the Imperial technical high schools at Stuttgart, Vienna, and elsewhere, such chairs exist, as well as at Upsala, in most of the Swiss and Belgian universities, and in some of the Italian. In regard to France and one or two other countries I have no definite information, but I think I have said enough to establish my point—that in many of the world's leading universities the teaching of analytical chemistry is entrusted to a specially appointed professor, who takes equal academic rank with his other chemical colleagues. Even when this is not the case, assistant professors or special assistants are frequently appointed to deal solely with this branch of chemistry. It clearly cannot be objected that it has not been our custom in this country to appoint professors to deal with special branches of chemistry, since in some of our colleges chairs exist devoted to physical chemistry, biochemistry, tinctorial chemistry, fuel chemistry, brewing chemistry, agricultural chemistry, technical chemistry, and metallurgy.

"I am not foolish enough to imagine that the establishment of chairs of analytical chemistry in all or any of our universities and colleges would bring forth a new heaven or a new earth, but at least it is certain that this highly important branch of chemistry would be taught under better conditions than those which in many cases exist at present. The teachers, being in a position to devote themselves entirely to their special branch of instruction, would be able to give more time and attention to the student, and surely in no branch of chemistry is close and constant supervision of practical work so necessary. They would also have the time to make themselves thoroughly conversant with their subject in both its theoretical and practical aspects, as well as to keep in touch with modern developments, and their laboratories might even become in process of time centres of original work in a department of our science in which research has been for so long neglected."

Since the above was written, some signs of progress auguring well for the future have been observable. That analytical chemistry is in a condition of vigorous growth I have endeavoured to show, and that it may continue to flourish exceedingly must be the earnest wish of every member of this Society. All the

branches of our science are reciprocally reactive and closely interdependent, and on the progress of British chemistry as a whole, and on the position which it holds in the national esteem, the future of this country, and indeed of the Empire itself, will to no small extent depend. May our rulers and our people be wiser in the future than they have been in the past.



## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

### FOOD AND DRUGS ANALYSIS.

**Estimation of Phenacetin when mixed with Acetanilide. R. Miller.** (*Amer. J. Pharm.*, 1917, **89**, 156.)—The method is based on the well-known nitric acid test for phenacetin of Autenreith and Hinsberg (*ANALYST*, 1891, **17**, 56), which gives an intense yellow to orange colour, and also upon the facts that phenacetin is soluble in methyl alcohol, and upon the addition of nitric acid to the suitably diluted solution the yellow colour is produced which, when compared in Nessler tubes with a standard phenacetin solution in methyl alcohol, serves to measure the amount present. Since methyl alcohol decreases the intensity of the colour, the same amount of the solvent must be arranged for in each tube compared.

H. F. E. H.

**Estimation of Novaspirin, alone or when mixed with Aspirin. R. Miller.** (*Amer. J. Pharm.*, 1917, **89**, 155.)—The method depends upon the fact that sodium hydroxide produces a yellow colour with novaspirin, but remains colourless with aspirin. The aspirin must not be present in a greater proportion than 2 parts of aspirin to 1 of novaspirin, or it interferes with the production of the yellow colour. Standard dilutions of novaspirin in 95 per cent. alcohol are made and compared with the substance under examination,  $\frac{N}{5}$  caustic soda being employed in the cold to produce the colour.

H. F. E. H.

**Estimation of Milk-Sugar in Headache Powders. R. Miller.** (*Amer. J. Pharm.*, 1917, **89**, 154.)—The method depends on the fact that milk-sugar when heated with ammonia gives a yellow to red colour, the intensity of which is used to measure the amount of sugar present. Standard dilutions representing from 5 to 25 mgrms. of milk-sugar are made, to which are added 10 c.c. of strong ammonia. These and the material under examination are then heated in a water-bath to about 95° C. for half an hour, and the colours produced compared in Nessler tubes, the final volumes in all cases being brought to 50 c.c. The powders should be previously extracted with a mixture of chloroform and alcohol to remove acetanilide, phenacetin, etc.

H. F. E. H.

**Analysis of Desiccated Milk. C. Porcher.** (*Ann. Falsific.*, 1917, **9**, 450-456.)—*Moisture.*—To prevent caramelisation it is best to estimate the moisture by drying the powder at 40° to 45° C. over phosphorus pentoxide. There is no advantage in speed in using a temperature of 60° to 70° C., the drying being almost complete at the lower temperature within forty-eight hours, or, if great accuracy is required, within seventy-two hours. *Fat.*—The method of extracting the fat with ether gives too low results, even when the extraction is continued for eight hours. The method of Röse-Gottlieb as modified by Richmond (*ANALYST*, 1908, **33**, 389) gives better results. For example, in the analysis of fifteen samples of desiccated milk of various origin the difference in the proportions of fat yielded by the two methods was usually over 1 per cent., and in one case was 3.40 per cent. Only one sample showed the same results (within 0.02 per cent.) by the two methods.

C. A. M.

**Estimation of Theobromine. L. Debourdeaux.** (*J. Pharm. Chim.*, 1917, **15**, 306-311.)—Maupy has described a method (*ANALYST*, 1897, **22**, 191) in which theobromine is separated from cocoa by extraction with a mixture of phenol and chloroform, evaporation of the solvent, and precipitation with ether; theobromine is insoluble in ether, whilst caffeine, colouring matter, and fat, are soluble. The precipitate of theobromine thus obtained is collected and weighed. It still contains from 6 to 12 per cent. of impurity, and the author therefore amplifies the method with the object of obtaining a residue of pure theobromine. One hundred grms. of the cocoa are mixed thoroughly with 40 c.c. of water (the addition of water is necessary, since phenol-chloroform does not extract the alkaloid from dry cocoa), and the moist mass is boiled under a reflux apparatus for two hours with a mixture of 60 grms. of crystallised phenol and 340 grms. of chloroform; after cooling, the solution is filtered, and the extraction with phenol-chloroform is twice repeated. The chloroform is then separated from the extract by distillation, and the dry residue obtained is mixed with 900 grms. of ether; after about eighteen hours the precipitated theobromine is collected on a filter, washed with a small quantity of ether, the filter and precipitate are boiled for a few minutes with a mixture of 20 grms. of sulphuric acid (sp. gr. 1.842) and 180 grms. of water, and the solution is filtered into a flask containing 250 c.c. of ammonia (sp. gr. 0.924), the filter being washed with hot dilute sulphuric acid. To the ammoniacal solution are added 3 grms. of silver nitrate, the solution is evaporated until all the free ammonia has been expelled, then diluted to 500 c.c. and set aside overnight. The silver-theobromine compound is collected, washed with about 250 c.c. of water, then mixed with 50 c.c. of water and decomposed with hydrogen sulphide; 600 c.c. of amyl alcohol are now added, and the whole mixture is distilled until about 200 c.c. of distillate (water and amyl alcohol) have been collected. The residual amyl alcohol solution in the flask is filtered while hot, the insoluble portion is washed with boiling amyl alcohol, and the filtrate is set aside at 15° C. for thirty-six hours. The crystalline mass of theobromine which separates out is collected on a filter, washed with ether, dried at 100° C., and weighed; the weight of the amyl alcohol must be noted and a correction applied for the solubility of the

crystals, since 1,000 grms. of amyl alcohol at 15° C. dissolve 0.200 grm. of theobromine.

The method has been applied to various cocoa products, and found to give trustworthy results. It is unnecessary to remove the fat previous to the estimation of the theobromine; when only small quantities of theobromine are present the amyl alcohol solution may be concentrated to a smaller volume than that mentioned.

W. P. S.

### BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

**Separation and Estimation of Butyric Acid in Biological Products. I. K. Phelps and H. E. Palmer.** (*J. Biol. Chem.*, 1917, **29**, 199-205; through *J. Soc. Chem. Ind.*, 1917, **36**, 567.)—The process described depends on the insolubility of quinine formate and quinine acetate, and on the solubility of quinine butyrate in carbon tetrachloride. Briefly, the solution containing the three acids is neutralised with barium hydroxide solution, a quantity of quinine sulphate sufficient to precipitate the barium is added, the barium sulphate is separated by filtration, and the filtrate is evaporated under reduced pressure; the residue obtained is then extracted with carbon tetrachloride, and the quinine butyrate recovered by evaporating the solvent. From 89.7 to 100.5 per cent. of the butyric acid present is found by the process. The solubilities of quinine butyrate and quinine propionate are so nearly alike that only a partial separation of these two salts can be effected, but the propionate may be separated readily from the formate.

**Detection of Protozoal Cysts in Fæces by Means of Wet Stained Preparations. R. Donaldson.** (*Lancet*, 1917, **192**, 571.)—The usual procedure for the detection of *Entamoeba coli* and *E. histolytica* consists either in a preliminary examination of a film in normal saline followed by Gram's iodine solution, or in the use of Gram's solution direct; in either case the iodine stains the food débris more or less deeply, and renders the detection of the cysts a matter of considerable difficulty. The author claims that the use of the following stains reduces the time spent very considerably, and renders it almost impossible even for a novice to overlook the cysts if present. A mixture of equal parts of the two stains used in any of the three following combinations yields the best results: A. Five per cent. aqueous solution of potassium iodide saturated with iodine to which is added an equal volume of either—B. (1) Saturated aqueous rubin S, or (2) saturated aqueous eosin, or (3) Stephen's scarlet writing fluid. Some brands of red ink are unsuitable, and basic fuchsin is unsuitable. The film to be stained with the above must be spread evenly and as thinly as possible, care being taken not to include any grosser particles, either whole or crushed. Such a preparation shows a more or less homogeneous red background, from which the cysts stand out as brilliant yellow or greenish-yellow spheres with a sharply defined outline, which in the case of *E. coli* and *E. histolytica*, when using the rubin S combination and daylight illumination, show a sharp deep purple ring. The nuclear structures stand out as prominently as in the case of the old simple iodine method. While not claimed as an absolute method of distinguishing *E. coli* from *E. histolytica*, experienced workers will, as a rule,

soon note sufficiently marked differences to enable an opinion to be expressed. The only other objects likely to stain similarly to the cysts are plant hairs and a few mould spores; while what are probably dead leucocytes stain varying tints of brown or greenish-yellow. All the other débris takes a more or less brownish tint, and bacteria remain practically unstained and unobtrusive. The best contrast is obtained by using daylight illumination and the rubin S combination.

H. F. E. H.

**Lipase in the Seeds of *Spartium Junceum*. M. Raffo.** (*Annali Chim. Applic.*, 1917, 7, 157-164.)—The seeds of the Italian broom *Genista (Spartium junceum)* contain a lipase which has a slight hydrolytic action upon fats in an acid solution, but a much more pronounced action in a slightly alkaline solution. The best results were obtained by treating 10 grms. of an oil (sesamé, cotton, olive, or arachis oil) with 0.5 gm. of the crushed seeds at 38° to 40° C. in the presence of 8 to 12 c.c. of  $\frac{N}{10}$  sodium carbonate solution. Under these conditions the fatty acids liberated by the enzyme were equivalent to about 19 c.c. of  $\frac{N}{10}$  alkali after ninety-six hours; but showed no material increase after further treatment. The lipolytic activity was not affected by the presence of antiseptic agents such as mercuric chloride and chloral hydrate. The seeds contained about 10 per cent. of a green, semi-drying oil with the following characters: Sp. gr. at 15° C., 0.9403; refractometer (Zeiss) at 25° C., 73.5°; acid value, 9.1; saponification value, 198.6; iodine value, 134; Hehner value, 89.85; Reichert value, 0.44. *Fatty acids*.—Sp. gr. at 17° C., 0.9208; m.-pt., 26.6° to 27° C.; and solidification-point, 21.3° C.

C. A. M.

### ORGANIC ANALYSIS.

**Estimation of Free Carbon in Coal-Tar. P. Falciola.** (*Annali Chim. Applic.*, 1917, 7, 152-157.)—In the method of Ceruti (*L' Industria Chim.*, 1911, 6) castor oil is used as a solvent for the hydrocarbons in coal-tar, but the author finds that other oils, notably olive, sesamé, and arachis oils, are more suitable for the purpose. About 5 grms. of the coal-tar are introduced little by little into 125 to 155 c.c. of olive oil, which has previously been heated to 140° to 160° C. The mixture is heated to 180° to 190° C., then allowed to cool to about 150° C., and filtered through a counterpoised filter. The carbon deposited at the bottom of the basin is again heated to 180° to 190° C. with 50 to 75 c.c. of oil, which is filtered as before, and the residue is now transferred to the filter by means of carbon tetrachloride or ether. Finally, the filter-paper is dried and weighed. The amounts of free carbon thus separated from Italian coal-tar of various types ranged from 9.0 to 26.7 per cent. Naphthalene is soluble in its own weight of olive oil at 65° C., whilst the solubility of anthracene is 5 per cent. at 100° C. and 40 per cent. in the boiling oil. Very similar results were obtained with other oils.

C. A. M.

**Composition of Power Gases. W. A. Tookey.** (*J. Soc. Chem. Ind.*, 1917, 36, 309-316.)—Data, in the form of curves, are given which support the author's view that the efficiency of an engine is independent of the chemical composition or

calorific value of the gas within wide limits, provided the composition is constant and the engine adjusted to give the best results on gas of that composition. With the scanty amount of attention which gas-engine users expect to have to give to their engines, constancy of composition is of the first importance, for if the composition varies, the proportion of gas to air and the instant of ignition, originally correct, will be incorrect, with consequent loss of efficiency, of power, and possibly with a tendency to dangerous pre-ignition. Whilst the efficiency of an engine is thus independent of the composition of the gas supplied to it, provided this be constant, the power developed by an engine is not independent of the composition of the gas, because a mixture of poor producer or blast-furnace gas with the best proportion of air contains less potential chemical energy per cubic foot than does a mixture of coal-gas with its best proportion of air; the lower rating of engines when used with poor gas is, of course, well known. The author purposely avoids the question of cost. Whether it is more economical to purchase and use coal-gas or manufacture and use producer gas is a question to be decided in every case by local conditions. The author expressly limits his discussion to the thermal efficiency of the engine.

G. C. J.

**Stannous Chloride Reduction Method for Estimating Nitrotoluenes.** E. de W. S. Colver and E. B. R. Prideaux. (*J. Soc. Chem. Ind.*, 1917, **36**, 480-483.)—The method described by Altmann (*J. Prak. Chem.*, 1901, **63**, 370) for the reduction of nitro compounds with stannous chloride, and subsequent treatment of the excess of stannous salt with alkaline tartrate solution until the white precipitate first formed is redissolved, does not give very satisfactory results in the titration. Titration with iodine gives numbers which do not agree with those obtained by titration with permanganate. In the case of sparingly soluble substances the necessity of adding alcohol to facilitate the initial reduction of the nitro compound by stannous chloride complicates the subsequent titration, and the possible reaction of the iodine or permanganate with the amino compound has also to be reckoned with. The use of the alkaline tartrate is objectionable because the rate of its addition has to be carefully regulated according to the degree of acidity of the stannous chloride. For these reasons it was thought desirable to effect the titration of the excess of stannous chloride with iodine in acid solution, thereby avoiding the use of the alkaline tartrate, the influence of the alcohol, and, to a large extent, the secondary reaction of the iodine with the amino product. A quantity of the nitro compound which will require about 10 c.c. of 2 N or 2.5 N stannous chloride solution is treated with 20 c.c. of this solution in a 100 c.c. flask, and 10 c.c. are measured out as a control in a similar flask. The two flasks are heated, shaken, etc., in the same manner, so that the difference in the atmospheric oxidation in the two cases is negligible. The contents of the flasks, with the addition of about 3 c.c. of strong hydrochloric acid, are heated in a boiling-water bath and shaken. In the case of di- and trinitro compounds a bright yellow colour usually develops, but disappears in a few minutes, leaving the liquid colourless or faintly yellow. After cooling and making up to 100 c.c., portions of the sample and the blank are diluted with water and titrated with iodine at the rate of about 2 drops per second.

It is important to add the iodine at about the same rate to both, as the quantity of iodine required is less for a slow titration than for a quick one. One blank will serve with sufficient accuracy for the duration of a working day. In dealing with such strong solutions of stannous chloride the ratios of the measuring instruments must be accurately gauged. The method appears to give with pure substances consistently low results, averaging 95 to 96.8 per cent. of the theoretical values, but it does not compare altogether unfavourably with the combustion method. For the determination of the composition of binary mixtures of the nitrotoluenes, using the iodine equivalents found, the method is quite promising, since the results are sufficiently constant under constant conditions of reduction and titration to indicate the composition of such mixtures within 1 per cent.

J. F. B.

**New Applications of Thymolphthaleïn and Naphtholphthaleïn.** J. Moir. (*J. Chem. Met. and Min. Soc., S. Africa*, 1917, **17**, 129-132; through *J. Soc. Chem. Ind.*, 1917, **36**, 571.)—The insensitiveness of thymolphthaleïn to traces of alkali, particularly at the boiling-point, has been utilised in the determination of lime and magnesia in limestone. 0.5 to 0.75 grm. of sample free from grit is mixed with about 10 c.c. of 2 N hydrochloric acid, the mixture heated on the water-bath for 20 minutes, the liquid diluted to about 20 c.c. and titrated with  $\frac{N}{2}$  caustic soda (free from carbonate), using a 0.02 per cent. methyl red solution in dilute alcohol as indicator; the combined acid equivalent of the lime and magnesia is thus obtained. After diluting to 50 c.c. and raising to the boiling-point for one minute, 3 c.c. of 1 per cent. thymolphthaleïn solution in 60 to 70 per cent. alcohol, and then sufficient  $\frac{N}{2}$  caustic soda to give a dark blue solution, are added, the mixture boiled for one minute to coagulate the precipitated magnesia, and the blue suspension titrated until yellow with  $\frac{N}{2}$  hydrochloric acid; in this manner the magnesia content is determined, and the lime may be obtained by difference. A correction should be made in case an appreciable amount of phosphate is present. The results agree closely with those found by the ordinary method.

In analysing the ammonium salts of strong acids, the solution, previously neutralised to methyl red if necessary, is titrated at the boil with  $\frac{N}{2}$  caustic soda in presence of a small quantity of a saturated solution of thymolphthaleïn in 50 per cent. alcohol until the deep blue to green colour reappears and withstands boiling for 20 seconds.

The true neutrality of water is determined by using as mixed indicators methyl red and *a*-naphtholphthaleïn, which are much more delicate than methyl orange and phenolphthaleïn, and will detect 0.1 part sulphuric acid and 0.2 part calcium hydroxide per 100,000. In presence of more than 0.4 part acid per 100,000, the colour is violet-rose; 0.2 part acid, salmon-orange; neutral, straw-yellow; 0.2 part alkali, citrine-green; over 0.4 part alkali, deep bluish-green. Neutral red, rosolic acid, or alizarin, may be used in place of methyl red.

**Estimation of Xylene in Solvent Naphtha.** P. E. Spielmann and F. B. Jones. (*J. Soc. Chem. Ind.*, 1917, **36**, 489-490.)—The method is founded on the fact that if the benzene, toluene, and xylene be completely removed by fractionation from solvent naphtha and the fraction of the residue boiling from 143° to 170° C.



be examined in a constant boiling-point apparatus, such as that devised by Northall-Laurie (ANALYST, 1915, 40, 384) in connection with the estimation of toluene, the constant boiling-point observed scarcely varies with different makes of solvent naphtha. Commercially pure xylene fractionated and collected between 138° and 143° C. gives in the same apparatus the constant boiling-point of 139.15° C., and it is possible from the examination of known mixtures of pure xylene with the 143° to 170° C. residue to construct a curve by which the composition of unknown similar mixtures may be estimated by their boiling-points. One hundred or 200 c.c. of solvent naphtha, accurately measured, are distilled through a Young's 12-pear still head at the rate of one drop per second. The fractions up to 138° C. and from 138° to 170° C. (all temperatures being corrected) are collected in separate cylinders and measured. The benzene, toluene, and xylene in the fractions up to 138° C. are estimated by Colman's methods, and the xylene in the 138° to 170° C. fraction is estimated by taking the boiling-point in the constant boiling-point apparatus and referring to the curve. In determining the boiling-point all possible precautions must be taken, and corrections made for barometric pressure, thermometer error, and unexposed stem. A steady temperature is usually attained after about twenty minutes' boiling at such a rate that the liquid drops back from the end of the condenser at the rate of one drop per second. The accuracy of the boiling-point curve may be taken as  $\pm 1.5$  per cent. when the xylene in the 143° to 170° C. fraction exceeds 50 per cent., but when only small quantities of xylene are present there may be an error of over 2.5 per cent. In practice, however, the percentage of xylene in solvent naphtha usually exceeds 50 per cent., so that the maximum error is seldom attained. The quantity of xylene found in the lower fractions by Colman's method is added to that estimated in the higher fraction by means of the curve, and the total xylene in the naphtha thus calculated.

*Estimation of Paraffin in Xylene.*—One hundred c.c. of the sample are distilled through a Young's 12-pear column at the rate of one drop per second, the portion distilling between 138° and 143° C. (corr.) being collected separately. Ten to 20 c.c. of this fraction are vigorously shaken for forty minutes with two and a half times its volume of weak "oleum," made by mixing 1 vol. of 22 per cent. oleum with 2 vols. of 95 per cent. sulphuric acid. The absorption of the aromatic hydrocarbons is carried out in a 100 c.c. flask with graduated neck. After sufficient shaking, the level of the liquid is driven up into the graduated neck by the addition of a further quantity of 95 per cent. sulphuric acid. After standing, preferably overnight, the paraffin will be found to be sharply separated. The quantity of paraffin found in 20 c.c. of the xylene fraction (138° to 143° C.) is calculated in proportion to the total xylene in the naphtha, and the value thus obtained is subtracted from the total xylene.

J. F. B.

### INORGANIC ANALYSIS.

**Detection of Calcium in the Presence of Barium and Strontium. Z. Karaoglanow.** (*Zeitsch. anal. Chem.*, 1917, 56, 138-141.)—Barium fluoride solution is used as the reagent, the test depending on the very sparing solubility of

calcium fluoride and the relatively greater solubilities of barium and strontium fluorides. One litre of water dissolves 16 mgrms. of calcium fluoride, 117 mgrms. of strontium fluoride, or 1,630 mgrms. of barium fluoride. A distinct turbidity is produced when the reagent is added to 10 c.c. of water containing 0.003 gm. of calcium chloride. The sensitiveness of the test is not affected by the presence of strontium chloride or ammonium chloride, but is diminished when the test solution contains barium chloride.

W. P. S.

**Colloidal Phenomenon as Indicator in Quantitative Analysis.** J. F. Sacher. (*Koll. Zeitsch.*, 1916, **19**, 276-277; through *J. Chem. Soc.*, 1917, **112**, ii., 180.)—In the estimation of lead by titration with a solution of ammonium molybdate, the supernatant liquid is turbid so long as the reaction is incomplete, but this turbidity disappears suddenly at the end-point. The turbidity is due to colloidal lead molybdate and the coagulation of this serves to indicate the end-point. In practice, the solution of lead, acidified with acetic acid, is heated to 70° to 80° C., and the progress of the titration is determined by removing a drop of the solution and observing its optical condition. The end-point is independent of the quantity of acetic acid present, and the method is to be preferred to the older procedure in which tannin is used as indicator.

**Differential Iodimetry. II.—Titration of Chromic Acid in Presence of Ferric Iron, and Estimation of Chromium in Chromite.** O. L. Barnebey. (*J. Amer. Chem. Soc.*, 1917, **39**, 604-606.)—Ferric iron reacts so slowly with potassium iodide in phosphoric acid solution (ANALYST, 1915, **40**, 365) that it is possible to estimate iodimetrically various oxidising agents in presence of ferric iron by regulating the acidity of the solution. In the case of periodates, iodates, bromates, and chlorates, boric acid was found to be the most suitable weak acid for the purpose (ANALYST, 1916, **41**, 106), but, to obtain a differential effect between chromic acid and ferric iron, phosphoric acid gives the best results. The minimum concentration of phosphoric acid for obtaining complete reaction with chromic acid is three minutes in the presence of  $\frac{N}{10}$ -iodide in 2.5 N-acid. If a longer time is allowed for completion of the reaction the minimum acidity is correspondingly reduced, though this is not desirable for titration purposes. A good method of oxidising iron and chromium is to make the aqueous solution just alkaline with sodium hydroxide, and then to add a slight excess of sodium peroxide. The solution is boiled to decompose this excess, and is then acidified with phosphoric acid, which is added in sufficient quantity to dissolve the iron phosphate and give a solution with a concentration of about 3N. Ten c.c. of  $\frac{N}{10}$ -potassium iodide solution are now added for each 100 c.c. of the solution, and the liberated iodine is titrated with standard thiosulphate solution. For the estimation of chromium in chromite the sample is fused with sodium peroxide, the mass extracted with water, and the excess of peroxide expelled by boiling. The solution is acidified with phosphoric acid to give a solution with an acidity of about 3N, potassium iodide added, and the liberated iodine titrated.

C. A. M.

**Differential Iodimetry. III.—Estimation of Available Oxygen in Soluble and Precipitated Oxidised Forms of Manganese.** O. L. Barnebey and W. C. Hawes. (*J. Amer. Chem. Soc.*, 1917, **39**, 607-610.)—Potassium permanganate solutions containing phosphoric acid can be accurately titrated by the iodimetric method in presence of ferric iron (see preceding abstract). The method is also applicable to the estimation of available oxygen in precipitated manganese dioxide and in the more easily decomposed pyrolusite ores. From 0.1 to 0.2 grm. of the sample of pyrolusite is treated with 10 c.c. of  $\frac{N}{1}$ -potassium iodide solution and 10 c.c. of 2N-phosphoric acid in an Erlenmeyer flask covered with a watch-glass, and the mixture diluted to 100 c.c. and left for ten minutes, after which the liberated iodine is titrated. It is essential that the sample should be of a sufficient degree of fineness to pass through a 200-mesh sieve, and if any undecomposed ore is left after the reaction it should be washed by decantation and again treated with phosphoric acid and iodide. Some varieties of pyrolusite, especially those containing iron oxide, cannot be analysed satisfactorily by this method, and a preliminary test should therefore be made to ascertain whether they react without difficulty. Manganese cannot be estimated by this method, owing to the fact that it cannot be precipitated as pure manganese dioxide, or that the excess of an oxidising agent cannot be successfully removed.

C. A. M.

**Separation of Iron from Lead.** J. F. Sacher. (*Chem. Zeit.*, 1917, **41**, 245.)—A method for the separation of small quantities of iron from lead depends on the insolubility of basic ferric nitrate. Two grms. of the lead salt are treated with a moderate excess of nitric acid (sp. gr. 1.15), the mixture is evaporated to dryness on a water-bath, and the residue is heated at 100° C. for fifteen to twenty minutes. The residue now contains the iron in the form of a basic nitrate of the approximate composition  $2Fe_2O_3 \cdot N_2O_5$ , or as a hydrate of this compound. Further heating results in a loss of nitric acid, so that the composition of the compound is not constant; but this is not of importance, as the iron still remains in an insoluble form. The residue is then treated with hot water, the insoluble portion is collected on a filter, washed, dissolved in hot dilute hydrochloric acid, and the iron is precipitated as hydroxide from the solution. Should the lead salt under examination contain silicates which are decomposed by nitric acid, the residue obtained after the evaporation of the nitric acid must be heated at 130° C.; lead nitrate is not decomposed at this temperature. If lead sulphate is present the basic iron nitrate must be extracted with hot ammonium acetate solution before it is dissolved in hydrochloric acid. The separation of iron from lead by the above method is so complete that the filtrate from the basic iron nitrate precipitate does not yield any coloration when tested with thiocyanate.

W. P. S.

**Titration of Magnesium.** F. W. Bruckmiller. (*J. Amer. Chem. Soc.*, 1917, **39**, 610-615.)—For the accurate estimation of magnesium by Stolba's method of titrating the precipitate of magnesium ammonium phosphate with hydrochloric acid it is essential that the solution from which the precipitation is made should be neutral, as free as possible from ammonium salts, and that the ammonia should

be added after the phosphate solution. The formation of the salt  $Mg_3(PO_4)_2$  is prevented by keeping the solution just alkaline while adding the precipitant, and that of the salt  $Mg(NH_4)_4(PO_4)_2$  by avoiding an excess of ammonium salts. In the analysis of waters the solution containing the magnesium is evaporated to dryness, and ammonium salts are removed by heating the residue, which is afterwards taken up with water acidified with hydrochloric acid, and filtered. The filtrate is made slightly alkaline with ammonia, a solution of microcosmic salt added slowly, with stirring, to the cold solution, and, after the precipitate has formed, a volume of ammonium hydroxide equal to a third of the total volume of liquid is added and the whole allowed to stand for eighteen hours. The precipitate is separated, with the aid of suction, washed with 25 c.c. of alcohol, then washed back into the beaker with hot water, and treated with a measured excess of  $\frac{N}{10}$ -hydrochloric acid, the excess of which is titrated with  $\frac{N}{10}$ -sodium hydroxide solution, with methyl orange as indicator. In estimating magnesium by precipitation as ammonium magnesium arsenate and the iodimetric titration of the precipitate a large excess of sodium arsenate must be used for the precipitation, whilst, in titrating the liberated iodine, the solution must be kept decidedly acid to prevent a reverse action taking place. The solution containing the magnesium is evaporated and freed from ammonium salts by ignition. The residue is taken up with a small quantity of hydrochloric acid and filtered, the solution cooled, and an excess of 10 c.c. of ammonia solution added. Sodium arsenate in an excess of 10 to 20 per cent. is next slowly added, with vigorous stirring, which is continued for about ten minutes until precipitation is complete. The precipitate is left to subside and is then collected, washed with 3 per cent. ammonia water, and dissolved in hot water. Ten c.c. of strong hydrochloric acid and 0.3 gm. of potassium iodide are added for each 100 c.c. of liquid, and the liberated iodine is titrated with  $\frac{N}{10}$  thiosulphate solution. Still better results may be obtained by the following modification of the method of Gooch and Browning (*Amer. J. Sci.*, 1890, **3**, 40, 66), in which the arsenious acid is titrated with iodine after removal of the liberated iodine in the original solution by boiling with sulphuric acid. The precipitate of magnesium ammonium arsenate, obtained as described above, is dissolved in hot water, an excess of potassium iodide and 10 c.c. of sulphuric acid (1:1) added to the solution, and the whole boiled rapidly in an Erlenmeyer flask, provided with a trap, until iodine vapours are no longer visible. The acid solution is neutralised with  $\frac{N}{10}$  sodium hydroxide solution, and phenolphthalein used as indicator, whilst from time to time sodium phosphate solution (11 grms. in 50 c.c.) is added, so that, after the titration is complete, the volume of phosphate solution added is equal to half the volume of the iodine solution. The volume should be about 250 c.c., and, if greater than this, more phosphate must be added to keep the concentration of the hydrogen ion at the right value. The arsenious acid is then titrated in the usual way with  $\frac{N}{10}$  iodine solution. The use of sodium phosphate and sodium hydroxide for the neutralisation is more effective than the sodium bicarbonate used in the original method for maintaining the correct concentration of the  $H^+$  ion.

C. A. M.

**Yellow Mercuric Oxide as a Standard in Alkalimetry.** G. Incze. (*Zeitsch. anal. Chem.*, 1917, **56**, 177-191.)—The use of yellow mercuric oxide is recommended for standardising acid solutions used in volumetric analysis; the oxide is free from water of crystallisation, and is not hygroscopic. W. P. S.

**Estimation of Phosphoric Acid and (Alkaline) Phosphates by Alkalimetric Methods.** J. H. Smith. (*J. Soc. Chem. Ind.*, 1917, **36**, 415-419.)—The substance is dissolved in a minimum quantity of distilled water, and phenolphthalein in small quantity is added. If no pink colour develops, trisodium phosphate and sodium carbonate may be assumed to be absent. The solution is heated to 55° C., and kept at this temperature during the whole of the titrations. The solution, if acid to phenolphthalein, is titrated with normal sodium hydroxide until a pink colour develops. The end-point is easier to determine if sodium chloride is present. Let the consumption of alkali in this titration be A c.c. The solution is next titrated back with  $\frac{N}{1}$ -hydrochloric acid, using methyl orange as indicator. Let the amount of acid required be B c.c. If A is greater than B, A - B is the measure of the free phosphoric acid present, and B that of the sodium dihydrogen phosphate. If, on the other hand, B is greater than A, B - A is the measure of the disodium hydrogen phosphate, and A that of the sodium dihydrogen phosphate. If A = B, either A or B is the measure of the sodium dihydrogen phosphate.

A third end-point, C, is obtained as follows: B c.c. of  $\frac{N}{1}$ -hydrochloric acid are added to the solution, which is boiled vigorously for fifteen minutes. This decomposes carbonates and converts metaphosphates into orthophosphates. The solution is then cooled to 55° C., B c.c. of  $\frac{N}{1}$ -sodium hydroxide are added, and the mixture then titrated with  $\frac{N}{1}$ -sodium hydroxide until the development of the phenolphthalein pink coloration. Let the consumption of alkali be C c.c. If C = B, metaphosphates and carbonates were certainly absent. If C is greater than B, metaphosphate was present, whilst carbonates cause C to be less than B.

With alkaline salts, free from carbonate and metaphosphate, A is the measure of the trisodium phosphate, if A is less than B, and B - A that of the disodium hydrogen phosphate; whilst if A is greater than B, B is the measure of the trisodium phosphate, and  $\frac{A-B}{2}$  that of the sodium hydroxide present in the sample.

When carbonates are present, and A is less than B, A + C - B is the measure of the triphosphate, B - A of the disodium phosphate, and B - C of the carbonate. If, on the other hand, A is greater than B, then B - C measures the carbonate, C the triphosphate, and  $\frac{A-B}{2}$  the hydroxide present.

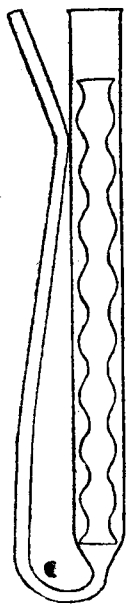
Similar schemes have been proposed before, but gave only very roughly approximate results. In studying the effect of temperature on the end-points, however, the author discovered that by working at 55° C. any alkaline phosphate present in a mixture of such phosphates could be estimated with an error not exceeding 0.5 per cent. G. C. J.

**Estimation of Phosphorus in Zinc Phosphide.** G. Liberi. (*Annali Chim. Applic.*, 1917, **7**, 144-151.)—The phosphide  $P_2Zn_3$ , which is that produced in the

normal reaction between phosphorus and zinc, is used in agriculture in the form of a greyish-black powder. For the estimation of the phosphorus 0.2 to 0.3 gm. of the sample is placed in a flask through which is passing a current of carbon dioxide, and is treated with 20 c.c. of water, and then slowly, from a thistle funnel, with 50 c.c. of dilute sulphuric acid (1:1). The hydrogen phosphide passes into a bulb absorption tube, and subsequently into a Peligot tube containing respectively 50 c.c. and 10 c.c. of a 3 per cent. solution of silver nitrate. Most of the gas is evolved in the cold, and finally the reaction is completed by boiling the liquid in the flask for about thirty minutes, whilst the current of carbon dioxide is continued for an additional thirty minutes. The yellow precipitate of  $[PAg_3 \cdot AgNO_3]$  is decomposed, when the liquid is diluted with water, into metallic silver, nitric acid, and phosphoric acid. The contents of the absorption vessels are transferred to a beaker, the vessels washed first with a little nitric acid and then with water, and the washings added to the liquid, which is then gently heated on the water-bath. The silver is precipitated by means of a slight excess of hydrochloric acid, the liquid evaporated on the water-bath nearly to dryness, then diluted with water and filtered, and the phosphoric acid in the filtrate is precipitated as ammonium magnesium phosphate in the usual way. The weight of magnesium pyrophosphate multiplied by the factor 0.2787 gives the quantity of active phosphorus in the zinc phosphide.

C. A. M.

#### APPARATUS, ETC.



**Simple Gas Absorption Apparatus.** H. D. Richmond and E. Hembrough. (*J. Soc. Chem. Ind.*, 1917, **36**, 317.)—The apparatus illustrated consists of two parts. The inner tube, made from tubing of 4 mm. internal diameter and about 15 cm. long, has eight bulbs of about 12 mm. diameter blown on it, and the ends are expanded into small funnels of about the same diameter. This tube lies within a tube of about 17 mm. diameter and 20 cm. long, the bottom being drawn out and sealed to an inlet tube of 3 mm. diameter, bent in the form of a U. In this tube is placed 10 to 15 c.c. of absorbing liquid; the gas enters by the inlet tube and bubbles up through the bulb tube, taking up some of the liquid right to the top of this, so that a very large absorbing surface is exposed. Experiments are described which show that the apparatus is more efficient than the "ordinary wash-bottle." The apparatus is easily made, easily cleaned, and not at all fragile.

G. C. J.

**New Acid Sodium Phosphate and its Action on Glass, Porcelain, Silica, Platinum, and Nickel Vessels.** J. H. Smith. (*J. Soc. Chem. Ind.*, 1917, **36**, 419-420.)—The new salt is easily prepared in an

impure state by evaporating mixtures of sodium hydroxide or carbonate with a sufficient excess of phosphoric acid and igniting the residue at a bright red heat. The salt is a fused, glassy mass, which dissolves slowly in cold,

but more readily in warm water. It appears to have the composition  $\text{Na}_4\text{P}_6\text{O}_{17}$ , but, in spite of the high ratio of acid to base, is nearly neutral to both methyl orange and phenolphthalein. On prolonged boiling with water it is converted into sodium metaphosphate and free orthophosphoric acid. Its corrosive action on glass, porcelain, platinum and silica is remarkable. At a red heat the glaze of porcelain is destroyed and a deposit of granular silica usually left; silica vessels are also attacked and platinum rendered so brittle that a dish which has contained the fused salt tears like paper. A nickel vessel was attacked until the residue consisted entirely of sodium and nickel pyrophosphates, the action being far more energetic than that of phosphoric acid alone or of metaphosphate, both of which attack nickel vigorously. The author proposes to call the new salt sodium polyphosphate.

G. C. J.

**Electro-Analysis using Silvered Glass Basins in Place of Platinum Cathodes.** J. Gewecke. (*Chem. Zeit.*, 1917, **41**, 297-298).—The silvering is effected as follows: The inner surface of a glass basin is ground by means of a sand-blast, and the basin is then washed, successively, with hot sulphuric acid and potassium bichromate mixture, sodium hydroxide solution, nitric acid, and water. To prepare the silvering solution, 8.5 grms. of silver nitrate are dissolved in 100 c.c. of water, ammonia is added until the precipitate first formed is nearly dissolved, the solution is filtered, and the filtrate diluted to 1 litre; 100 c.c. of this solution are mixed with 2 c.c. of 40 per cent. formaldehyde solution, and the mixture is immediately poured into the glass basin. The silvering is completed in about ten minutes, and the basin is then carefully washed and dried. A thin strip of platinum foil is now bent over the edge of the basin so as to make contact with the coating. After use, the basins are treated with nitric acid, washed, and then re-silvered.

W. P. S.



## OFFICIAL ORDERS.

### COMMONWEALTH OF AUSTRALIA.

#### IMPORTATION OF PEPPER.

THE Board of Trade have received copy of Statutory Rules No. 47 of 1917, dated February 28, 1917, which have been issued under the "Commerce (Trade Descriptions) Act, 1905," and which amend the previous Regulations issued under that Act (Statutory Rules No. 347 of 1913), with effect on and after June 1, 1917.

The amending Regulations provide that, in addition to the prescribed "trade description" which must be applied to all articles of food for man before their importation into the Commonwealth is permitted, in the case of pepper berries (*Piper Nigrum*, L.) the "trade description" shall specify whether they are white or black.

The following Standards are added by the present Regulations to the list of Standards specified in the First Schedule to the original Regulations—viz.:

“Black Pepper”: Black Pepper is the dried immature berry of *Piper Nigrum*, L.; it shall contain—

- (a) No foreign substance;
- (b) Not more than
  - (1) 5 per cent. white berries,
  - (2) 15 per cent. of waste material,
  - (3) 7 per cent. of total ash;
- (c) Not less than
  - (1) 6 per cent. of extract soluble in ether, and
  - (2) 8 per cent. of extract soluble in ethylic alcohol.

“White Pepper”: White pepper is the dried more or less mature berry of *Piper Nigrum*, L.; it shall contain—

- (a) No foreign substance;
- (b) Not more than
  - (1) 5 per cent. black berries,
  - (2) 7 per cent. of immature berries,
  - (3) 3·5 per cent. of ash;
- (c) Not less than
  - (1) 6 per cent. of extract soluble in ether, and
  - (2) 7 per cent. of extract soluble in ethylic alcohol.

It is provided in the Regulations of 1913, which are still operative, that the importation of all goods mentioned in the First Schedule above referred to, which do not comply with the Standards set out therein, is prohibited, unless the trade description applied to the goods includes in bold and legible characters the matters and the extent to which the goods do not comply with the standards applicable thereto.—*Board of Trade Journal*, May 24, 1917.



### REVIEWS.

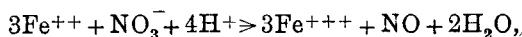
ANALYTICAL CHEMISTRY. VOL. I.: QUALITATIVE. By TREADWELL and HALL. Fourth English, based on the Eighth German Edition. Pp. 538. John Wiley and Sons (Chapman and Hall, Ltd., London), 1916. Price 12s. 6d. net.

In dealing with so progressive a science as chemistry it is not altogether an advantage to arrange a fresh edition of a work which has already established its position many years ago rather than to write an entirely new one. The electronic and electrolytic theories especially cannot be neglected by the student if he is to interpret reactions in accordance with modern views. Such theories must be clearly explained in any new textbook, and it must be shown that they illuminate facts consistently. All this requires much amendment of the language in which reactions were erstwhile presented. And this satisfactory statement of the foundation theories, with the subsequent exemplification of them in the reactions upon

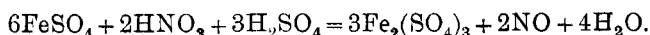


which analytical chemistry depends, may be taken as the leading, novel feature of this fresh edition.

Ionic equations are very generally used, and not infrequently reactions are expressed both by molecular and ionic equations, thus challenging a comparison. For instance, on p. 31, the reaction between a ferrous salt and nitric acid is shown alternatively as



or,



If the former is more educational, the latter presentation is nevertheless more convenient as indicating the materials which the chemist weighs or handles before solution is effected.

The scope of the work may be gathered from a statement of its sections. Part I. (76 pp.) is devoted to fundamental principles. Part II. (206 pp.) details the reactional properties of the ordinary metals or cations, which are arranged in the conventional five groups. Part III., occupying 137 pp., deals similarly, in eight groups, with the acids or anions. In the 33 pp. of Part IV. the student is led to subject unknown substances to systematic examination. If the volume is to serve as a practical textbook at the bench, this part will probably be referred to more often than any other, and it may be questioned whether the different group tables, now found—and quite rightly found—in other parts of the book, could not be repeated here on consecutive pages for the student's convenience. Part V. (66 pp.) deals with the rarer metals.

It is Part I., devoted mainly to the physical and electrical foundations of inorganic chemistry, which shows the greatest expansion as compared with previous editions. For this part it would seem that Professor Hall is mainly responsible, and there cannot be two opinions as to its cardinal importance. What is more open to question is whether it is properly placed in a work on qualitative analysis. Already the authors have separate volumes on *Qualitative Analysis* and *Quantitative Analysis*; and we would suggest that Part I. in this *Qualitative* volume, dealing with the general and fundamental principles, should be published separately in an expanded form: it is well worthy of an independent volume. It is subdivided into two sections: one dealing with Reactions in the Wet Way, explained by electrical theories, and the second dealing with Reactions in the Dry Way, as to which no such attempt at explanation is made.

After the elaboration with which the wet reactions are regularised by reference to electrical and physical theories, the dry way reactions emerge suddenly as belonging to a primitive age of chemistry. For it suffices here to distinguish between the oxidising and reducing portions of the flame, to be armed with a bit of charcoal—by preference such as obtained from an old-fashioned brimstone match—some fluxes, and a platinum wire! Mixing can be done on the palm of the hand by means of the pen-knife. Beads are moistened by the tongue, and to promote the evolution of phosphoretted hydrogen we are told to breathe over the mass. In these days of democratic reaction we are told how to distinguish the noble metals, and how to subdue these by *aqua regia*. The whole seems so human! Is it too

late to put a ring-fence round this dry way, with all its medieval charms? To forbid the ionist and the electronist to trespass here?

The other section, on Wet Reactions, is intended to direct the student's mind into the right ways of regarding chemical activity in solution. It deals with electrolytic dissociation, conditions of equilibrium and mass action; also with hydrolysis and colloidal solutions. There are valuable tables showing the degrees of ionisation of bodies in solution, of the E.M.F. or oxidation potentials, and of the limits of solubility and "solubility products." From the latter we learn that if we were given the solubility in water of the sulphide of an unknown metal, we could decide whether it would belong to the hydrogen sulphide group (Group II.), or to the ammonium sulphide group (Group III.)—the sulphides of the former being the more insoluble.

The phenomena of oxidation and reduction are also dealt with in this part—perhaps not altogether happily. Thus we are told that the atom consists of positively charged corpuscles and negatively charged corpuscles or electrons; that the unit negative charge or electron is so small that it may easily be lost; that, indeed, the negative electric charge is alone transferred, and the only way an element can be left positively charged is by losing one or more negative electrons. From this comes the electronic theory of oxidation and reduction: an element is *oxidised* when it loses an electron; it is *reduced* when it receives one. Here, then, we are given a simple and tangible mental image of what takes place, and it is a pity that this simplicity is not always reflected in the language—for example, in the following definition on p. 28: "Oxidation is the increase in the valence of an element or radical in the positive direction; reduction is the increase of the valence of an element or radical in the negative direction;" and a few pages later, in dealing with the oxidising power of hydrogen peroxide, we are told that the "peculiar atom of oxygen loses its positive charge and receives in its place a negative charge!" Incidentally, the oxidation theory leads to the conclusion that when a metal is dissolved by an acid the hydrogen acts as an *oxidising* agent.

The useful reactions for qualitative analysis are all gathered (p. 26) into four classes. Ought not another class to be added to comprise those instances in which a complex ion is formed associated with a change of colour?

We are glad to see the recommendation to have all the qualitative reagents made up in definite strengths quotable in terms of normality. This proposal was (as stated by the authors) first published by Blochmann in 1890. It had already been worked out in considerable detail, however, in this country by Reddrop in the Crewe Laboratory, about thirteen years previously, and a proposal made by him (vide *Chemical News*, 1890, p. 245) is worthy of adoption. In the Normal Equivalent system he retains the initial N for *accurately standardised* reagents, but for all the unstandardised reagents, which are only of approximate normality, he adopts the second initial letter, E. Thus, in the table on p. 71, where the authors tell us that sulphuric acid of 1.84 sp. gr. is of "36 N approximate concentration," Reddrop would simply say it is 36 E, and so on. By the way, in the table, a saturated solution of sulphur dioxide is stated to be of 0.33 N strength; it should be 4 E.

There is a very good coloured spectroscopic chart as a frontispiece. And the spectroscope is adequately described; but, peculiarly, this appears, not in Part I., but under the heading of Barium.

In the estimation of arsenic by the evolution of  $\text{AsH}_3$ , no reference is made to the work of Chapman and Law (*ANALYST* for 1906, **31**, 3; 1907, **32**, 250) on "Super-tension" of hydrogen dependent upon its means of generation. This is essential towards understanding the difficulties or uncertainties which otherwise attend the quantitative evolution of arsine, and certainly, serves as a valuable guide in the laboratory.

The volume is well arranged and clearly printed. The type errors which have come to our notice are rare; for the use of the authors in preparing fresh editions we may point out a few: On p. 13 we are told it requires only "0.0015 grm. of  $\text{AgCl}$  to form a saturated solution in water," the volume of the latter not being given; similar amendment is desirable on p. 12. On p. 24  $\text{AgNH}_3\text{Cl}$  appears instead of  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . On p. 43 the oxidation potential of copper to cuprous ions appears to be given in the table as  $-0.51$ , and in the text as  $-0.17$  volts. On p. 49 the valency of the first formula needs adjusting; an amendment, too, is necessary in the reactions on pp. 78 and 167. In the illustration on p. 91 the retort, from which ammonia is being distilled, has its neck closed at the end.

But the defects of the work are very few and of no serious significance. What is of significance is that we have here an admirable work on qualitative analytical chemistry, based upon physical theories, such a work as may be commended confidently to every serious student of chemistry.

J. H. B. JENKINS.

**EXPLOSIVES.** By ARTHUR MARSHALL. Second Edition in 2 volumes. Churchill, 1917. Price £3 3s.

It is now over twenty years since Mr. Guttman published his well-known "Manufacture of Explosives," and the need for a comprehensive work on the subject, comprising the more recent advances, has been frequently felt, especially in view of the great developments in the use of nitro-aromatic compounds since the date of Mr. Guttman's book. Mr. Marshall has based his work on a somewhat similar plan, but has greatly extended its scope, and covers practically the whole range of explosives in considerable detail. The wide appreciation which the work has met is shown by the appearance of a second edition within a very short time of the first, and Mr. Marshall has taken the opportunity to enlarge the work still further. The new edition comprises two large volumes, of which one has just appeared and the second is in the press. Progress in explosives is so rapid at present that a still more expanded edition may doubtless be looked forward to in the future.

The book made its appearance very appropriately at a time when many workers were turning their attention for the first time to the subject of explosives in consequence of the War. Mr. Marshall's position as Chemical Inspector to the Indian Ordnance Department, and his long experience of explosives entitle him to speak with authority, and he has collated a large fund of information in a way which renders his book most useful for reference.

Commencing with an instructive historical survey of explosives, the author proceeds to describe the manufacture of the principal explosives and the raw materials from which they are made. Black powder and several allied explosives are dealt with first, and the following chapters deal with sulphuric and nitric acid, which form necessary materials for all nitrations. Further information might with advantage have been given on the manufacture of oleum in the chapter on sulphuric acid. The important subject of synthetic nitric acid is briefly dealt with, and an extension of this section of the work would form a welcome addition to a future edition. Useful information on the manipulation of acids and the treatment of waste acids is given, and a number of tables are included.

Nitrocellulose and nitroglycerine are dealt with in detail as regards their manufacture and purification, and a useful collection of the researches on cellulose and its nitration has been included.

The nitro-aromatic compounds have hardly been dealt with so thoroughly as their increasing importance demands. Their methods of manufacture have developed enormously in the last few years, but the most recent developments could not, of course, be made public. The description of the trinitrotoluene manufacture is based mainly on Langenscheidt's description of 1912, and the description of the picric process differs also considerably from current practice.

The various types of mixed explosives are described, and the modern methods for the determination of the explosive constants are dealt with in detail. These include the calorimetric value, pressure of explosion, rate of detonation, sensitiveness to impact and friction. The chemical stability is of special importance, and has formed the subject of numerous researches which are recorded at some length.

An important chapter is devoted to the analysis of the materials which are used in the manufacture of explosives, and a collection of the methods used in this connection will be convenient for reference. Nitroglycerine and nitrocellulose and their raw materials have received the fullest notice. In the case of the nitro-aromatic compounds the information is somewhat limited, and more detail would have been welcome. A wide range of other materials is included, such as acetone, mineral jelly, etc., which are used incidentally in explosives. In view of the importance of nitric and sulphuric acid in all nitrations, more detailed descriptions of the analysis of the mixed acid and waste acids would be of value to the explosive chemist. Several appendices are added which aid in making the book complete as a book of reference for workers in explosives.

R. C. FARMER.

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#### ERRATA.

Page 200, line 14, *for Mitchell read Twitchell.*

Page 202, line 16, *for Castor Oil 10·4 to 0·7 read 0·4 to 0·7.*

