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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 2nd, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of:—Ernest Edward Unwin Abraham, B.Sc., F.I.C., Enid A. M. Bradford, B.Sc., Frank Brookhouse, B.Sc., A.I.C., Gerald Harry Edwards, B.Sc., A.I.C., Jack Firth, A.I.C., Albert E. Fletcher, F.I.C., Patrick Sarsfield MacMahon, M.Sc., F.I.C., Moses Puffeles, Edgar Alexander Raynor, B.Sc., A.I.C., Bernard Joseph Styles, Viscount Tiverton, Cecil Edgar Wiseman, B.Sc., A.C.G.F.C.

The following were elected Members of the Society:—Lionel James Dent, B.Sc., Leonard Arthur Haddock, B.Sc., A.I.C., Arthur Littlewood, M.A., A.I.C., and John Henry Weber, B.Sc., A.I.C.

The following papers were read and discussed:—"Observations on Changes in Raspberries after Picking," by Theodore Rendle; "The Separation of Uranium from Tantalum, Niobium and Titanium," by W. R. Schoeller, Ph.D., and A. W. Webb (*Work done under the Society's Analytical Investigation Scheme*); "A New Form of Filter Stick: Its Use in Gravimetric Analysis," by A. J. King (demonstrated by Janet W. Brown, Ph.D., A.I.C.); and "A New Method for the Iodimetric Titration of Phenols," by F. J. Warth.

Obituary

ALFRED CHASTON CHAPMAN

By the death of Alfred Chaston Chapman, on October 17th, 1932, a notable and greatly-esteemed figure in the chemical world has passed from our midst.

His attainments in the realm of chemical science, and more particularly in the domains of analytical chemistry and the brewing industry, mark him out as one of the most brilliant workers we have had during the last 40 years, and, as a pioneer in analytical chemistry within this period, he can rightly be classed with such "giants" as Alfred H. Allen and Otto Hehner.

In addition, however, to his achievements in these spheres, Chapman did what few other professional men of his time succeeded in doing, as he was able to convince the theoretical and purely scientific worker that analytical chemistry, while it might be followed as a profession, had yet a place as a true science and could contribute materially to the advancement of chemical knowledge. Chapman, indeed, by his example, helped to raise the profession of analytical chemistry to a position where it commanded recognition from the whole chemical and scientific world. Hitherto it had been too much the habit to regard the analytical chemist as one who pursued his practice, not with the idea of advancing science, but mainly for his own emolument. Chapman, by his work in various branches, not merely gained the professional success which his labour merited, but pursued his work in a genuine scientific spirit, having before him the attainment of truth and the advancement of his science.

Such an achievement has succeeded in putting the entire branch of analytical chemistry on a different footing from that which it occupied at the time he began his work, and Chapman has laid the whole class of professional chemists under a deep obligation to him for the unique services that he rendered.

The Society of Public Analysts, in particular, has reason to be profoundly thankful to him for what he did in their interests, and the present tribute to his memory is written by one who was his contemporary during all his working period, but who feels himself able to speak but inadequately of the influence for good which Chapman exercised and of the way in which, by his conduct and example, he succeeded in raising to its right position the profession to which they equally belonged.

But, besides the prosecution of his own practice to such useful ends as were accomplished, Chapman did a great deal more, in that he set a high standard of professional conduct and further devoted his energies and means to the advancement of the interests of his professional brethren. This he was enabled to do, not merely through his eminence in his particular branch of science, but by his personal character, his high sense of honour, and those qualities of kindliness, consideration, and sound judgment which endeared him to all who knew him, besides making him, in numerous spheres, an able and valued public servant.

Chapman was essentially a strong man, one who could speak and act forcibly, whose utterances, delivered clearly and concisely, carried conviction with them by their evident honesty of purpose, and it is no wonder that he was early selected to be Chairman of many scientific, professional, and industrial associations, and rendered valuable help in Government and other public enquiries.

The closing ceremony of October 20th was a fitting tribute to the esteem and affection in which Chapman was held by his scientific and professional brethren, who gathered there in representative capacity on behalf of the various organisations with which he had been connected, as also in their personal capacity. The Society of Public Analysts and Other Analytical Chemists naturally was well represented.

Since the journals and periodicals of other Societies have dealt with Chapman's life and work more particularly as regards his connection with them, it is fitting that the present record should be concerned mainly with his work in the analytical field, and his association with the Society of Public Analysts. Of the latter he became a member in 1895, served on the Council in 1897–8, was secretary in 1899, and continued to hold this office until his elevation, in 1914, to the Presidency, which position he occupied for the usual biennial period.

Born in 1869, Chapman received his early education at Leeds Grammar School; then, on the family coming to London, he began his chemical training at University College, London, his teachers being Professors Alexander Williamson and Charles Graham, with the latter of whom he was subsequently closely associated. At University College he became demonstrator in chemical technology, and, after a short period as assistant to Graham, he took the step of setting up for himself in practice as an analytical and consulting chemist. None but a man of determined energy would in those days have ventured on such a course, but this, Chapman—with a truly scientific aim before him and the will to succeed, aided, no doubt, by the possession of a financial competency—essayed to do, and began work in Leadenhall Street, primarily in relation to the brewing industry. It was not long before he established a practice for himself, and soon had to move to larger premises in Duke Street, Aldgate, where he remained until the close.

He not only built up a successful practice, at first chiefly connected with the brewing industry, but he was soon surrounded by a number of pupils, who found in him a ready and able teacher, and, under his guidance, frequently passed to positions of responsibility. Not only was Chapman thorough in his teaching, but he was imbued with the true spirit of scientific enquiry, so that, whilst he came to be an authority in the brewing world, his independent research work, which mainly occupied his interest, found its outlet in many different fields. Hence we find him working at the problems of fermentation generally, and his contributions to the literature of that division of chemistry are of the highest value. In particular, his researches on the essential oil of hops and its antiseptic significance excited much attention, while in later years the problems of bio-chemistry engaged his interest closely.

Very shortly after starting practice on his own account as an analytical and consulting chemist, Chapman began the series of contributions to technical, analytical and chemical journals which continued to the end of his career. His earliest writings were on matters connected with brewing, and were contributed (from 1893 on) to the *Journal of the Institute of Brewing*. Of these, the most important, perhaps, were those on the "Essential Oil of Hops" (1895, 1898, 1903, and 1929). His work on the preservative properties of hops is well known; he elaborated biological methods for the determination of the preservative value of hops and also methods for the determination of tannin (1907–9). The Standardisation of Analytical Methods in relation to the analysis of brewing materials formed the subject of other papers sent to the *Journal of the Institute of Brewing*.

Chapman commenced his written contributions to THE ANALYST in 1899 with a paper on the quantitative separation of isovaleric and acetic acids. This was followed, in 1900, by one putting forward a method for distinguishing hops and quassia. The same year (1900) came the notable arsenic "scare," which led to the appointment, in 1900, of a Royal Commission on Arsenical Poisoning in Food, before which Chapman gave evidence. In the report of the Royal Commission (1902) a general maximum for the proportion of arsenic in food was laid down, and it was shown that the Marsh–Berzelius test, as modified by Chapman and others, was capable of detecting far less than this proportion.

In this connection Chapman did much valuable work which greatly assisted the Royal Commission, and he contributed to THE ANALYST a number of papers on the methods of determining arsenic (1901, 1904, 1906, and 1907), these culminating in 1907 with his discovery that the coating with cadmium of the zinc used in the Marsh–Berzelius method for determination of arsenic, removed the difficulties that had been so frequently experienced with regard to the "insensitiveness" of the zinc.

While it is for his contributions to the subject of the determination of arsenic and the methods that he devised in that connection that analytical chemists will mainly remember his work, his researches covered a far wider field in the domain of analytical chemistry.

Thus, we find him dealing extensively with essential and other oils from various sources. Already, in 1900, he had sent to THE ANALYST a communication on an improved absorption apparatus for use in the analysis of essential oils, followed, in 1907, by a note on camphorated oil, and a paper in 1912 on the examination of Chinese and Japanese wood oils. Later he turned to the examination of fish oils, and papers on the occurrence of hydrocarbons in fish-liver oil, on dog-fish liver oil, and on liver-oil of the tope, appeared in THE ANALYST in 1917, 1918, and 1922, respectively.

Nor must his communications to the *Journal of the Chemical Society* on spinacene and its derivatives (1917, 1918, and 1923) be forgotten. In these, mention is made of the curious hydrocarbon which he had found to constitute nearly 90 per cent. of the oil yielded by the livers of certain shark-like Mediterranean fish.

His work on the essential oil of hops, in particular, was of a high order, and contributed largely to our knowledge of their action and value. Papers on this subject and on fermentation in general naturally found a place primarily in the *Journal of the Institute of Brewing*, but several on this and allied subjects occur also in the *Journal of the Chemical Society* (1895, 1903, 1914, 1928, and 1929).

Yet other subjects on which Chapman wrote in THE ANALYST were Methods for the Estimation of Tartaric Acid (1907) and of Creatinine (1909), Malt Vinegar Standards (1912), Detection and Separation of Dye-Stuffs (1912), and (1926) the presence of arsenic and of lead and other metallic impurities in crustaceans and shellfish.

Chapman took a great interest in the advance of bio-chemistry as a separate branch of science, and, in addition to his earlier work on fermentation, he contributed papers on the nature and action of yeast, and on certain species of fungi. He was, indeed, the first (1926) to advocate the establishment of an Institute of Industrial Micro-biology, a hope that has not, as yet, materialised.

This by no means exhausts the list of Chapman's contributions, but will serve to indicate the great activity he displayed and his desire to add to chemical knowledge in practical directions.

Just as Chapman's tenure of the Secretaryship of the Society of Public Analysts was marked by much activity and a decided advance of the Society, so, too, his occupancy of the Presidential chair during the years 1914 and 1915 is memorable on two special accounts—the first, his Presidential addresses at the close of each session; and the second, the impetus given to the Analytical Investigation Scheme of the Society, which has materially assisted in the accomplishment of much good work by members of the Society, and has greatly enhanced the value of the pages of THE ANALYST.

This scheme was originally suggested by Chapman in 1904, when he was Secretary, and it met then with a fair success, papers embodying work carried out under it being, from time to time, contributed to THE ANALYST. But it was when Chapman became President that the scheme was more actively worked, and the co-operation of university professors and teachers was enlisted in its support. It can, indeed, now be regarded as an integral part of the Society's operations.

Chapman, while still Secretary, had represented the Society at the International Conference on the Unification of Methods of Food Analysis, held in Paris in 1910, and, not long after coming into office as President, found himself faced by the many difficult problems arising out of the war. In these, so far as his own science was concerned, he notably bore his part, concerning himself in particular with such matters as the supply of apparatus and reagents of British make.

In 1914 also, during his Presidency, the first joint meeting with the newly-formed Biochemical Society was held.

The addresses which Chapman gave at the close of each session of his tenure of the Presidency were masterpieces of their kind, and, in his insistence on the recognition of analytical chemistry as a branch of science and as calling for the establishment of Chairs of Analytical Chemistry in Universities and Colleges, he rendered lasting service to the cause he had at heart. But, perhaps, even more than this, his addresses—and more particularly that given on his relinquishing his office of President in 1916—constituted most able and powerful expositions of the work that analytical practice had been able to accomplish in late years, and of the position which it should occupy in the future.

It is not surprising, albeit a source of much satisfaction to all who had known him and his work, that this was followed by his election to the Fellowship of the Royal Society in 1920, largely as a result of his contributions to analytical chemistry.

To detail the many offices that he held and the various Enquiries and Commissions on which he served, would be but to repeat what has been already set out elsewhere. To the professional chemist it will suffice to record his services as Examiner, and later (1921–4) as President of the Institute of Chemistry, and the ever-ready support which he gave to all professional objects that called for his help.

Chapman's personality was a lovable one, and, backed up, as he was, by his able and energetic wife, and aided by his own high sense of honour and his sound judgment, he was privileged to confer, in the comparatively short period of his life, great and lasting benefits on the profession of which he was so eminent and esteemed a representative.

J. A. VOELCKER

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIV. An Improved Method for the Separation of Tantalum from Niobium

BY W. R. SCHOELLER, PH.D.

(Work done under the Society's Analytical Investigation Scheme)

THIS Section furnishes another instance of the progressive refinement we have been able to introduce in our methods as the result of continued study and practical application. In Section IV (ANALYST, 1925, **50**, 485), Powell and Schoeller described a new method for the separation of tantalum from niobium, this being the first application of tannin to the quantitative separation and determination of the earth-forming elements. Whilst that method is quite sound, there is, no doubt, some justification for the criticism that the original directions are rather involved; further, some of the recorded errors are unduly and unnecessarily high (we did not suppress any of the less favourable results); again, compensation of errors may have contributed to the apparent success of some of the tests. As it happened, the most difficult separation problem capable of being solved by the application of tannin was also the first to be studied; subsequent adaptation of the new procedure to other separations (*e.g.* XXIII, ANALYST, 1932, **57**, 550) led to an improved technique. This paper gives a concise description of the standardised fractionation process, as well as some examples of its practical application, which should prove a further help to those desiring to become familiar with the operation.

RATIONALE OF METHOD.—It is assumed that the operator is acquainted with the chemistry of the process. Suffice it to recall that tantalum and niobium are completely precipitated by excess of tannin from their oxalate solution on neutralisation with ammonia, but by carefully regulated addition of the two reagents it is possible to effect a separation, tantalum being precipitated from slightly acid solution. The tantalum-tannin complex is yellow, the niobium complex red; co-precipitation of niobium with the tantalum is indicated by the orange colour of the tannin precipitate. Fractional precipitation is unavoidable, because the tantalum cannot be quantitatively precipitated without considerable contamination with niobium if the tantalum concentration is lower than the niobium concentration.

The standardised procedure furnishes three fractions, namely, (i) a niobium-free tantalum fraction (yellow precipitates); (ii) a mixed or intermediate fraction (orange to red precipitates); and (iii) a niobium filtrate free from tantalum. (With low Ta:Nb ratios, a yellow precipitate will not be obtained in the first fractionation.)

Quantitative separation is achieved by *systematic re-treatment of the mixed or intermediate fraction*; this is fractionated as before, yielding another three fractions, the intermediate of which is fractionated in its turn (and so on, if necessary). All the yellow, pure tantalum precipitates are ignited together; the pure niobium filtrates are combined.

After one or two fractionations the intermediate fraction will have been reduced to something of the order of 0·02, or even less than 0·01, grm. If the operations are properly performed, the total error will be confined to that incurred in the final treatment of the last intermediate fraction. At that stage it is necessary, in order to counteract incomplete recovery of the tantalum, to produce a slightly niobiferous final tantalum fraction (*i.e.* pale orange precipitate). This conforms with the principle I have previously applied in the determination of platinum: "If a substance cannot be precipitated quantitatively in one operation without undue contamination, it may be feasible to obtain it in two fractions. The first or major fraction should be pure. The minor fraction completes the precipitation; it is not pure, but, if sufficiently small, it renders the error negligible for practical purposes." (ANALYST, 1930, **55**, 550.)

Reagents.—Potassium bisulphate, silica-free. Ammonium oxalate, saturated solution. Ammonium chloride, saturated solution. Tannin, freshly prepared 2 per cent. solution. *N* ammonia. Wash-liquor for tannin precipitates: 2 per cent. ammonium chloride. All reagents should be free from calcium salts.

Apparatus.—Tared silica crucible *s* for bisulphate fusion. A pair of fractionation beakers (600 c.c.; smaller size for end-fraction). Tared porcelain crucible, *p*, for tantalum precipitates. Squat beaker *B* (800 c.c.), for niobium filtrates. Apparatus for suction filtration (platinum or hardened paper cone). Whatman filters No. 40, 12·5 c.c. and smaller. For the smaller precipitates, simple filtration through Whatman No. 41 paper. Filter pulp. Burette for tannin (cf. *Manipulation, ignition, and leaching of tannin precipitates*: XIX, ANALYST, 1931, **56**, 308).

Notation.—The precipitates obtained in the first fractionation are designated, in succession, P^1, P^{1a}, P^{1b}, P^{1c}; those obtained in the second fractionation (*i.e.* re-treatment of the first intermediate), as P^2, P^{2a}, P^{2b}; those from the third fractionation (re-treatment of the second intermediate) as P^3, P^{3a}, P^{3b}, etc.

The Separation.—The mixed pentoxides (0·2 to 0·3 grm., or more if poor in tantalum) are fused with potassium bisulphate in the crucible *s*, and the product is dissolved in hot ammonium oxalate solution (75 to 100 c.c.). Any small residue is filtered off and re-treated, and the resulting solution (filtered if necessary) is added to the main portion.

FIRST FRACTIONATION.—The boiling solution (250 c.c.) is cautiously titrated with tannin reagent; if this produces a yellow coloration, enough tantalum is present to yield a yellow (niobium-free) P^1, provided the addition of tannin is interrupted before the yellow tint deepens to orange; see (*a*). If, however, an orange or red coloration is produced, P^1 will contain niobium as well as tantalum; see (*b*).

(*a*) *The Coloration is Yellow*.—Four precipitates are produced in the first fractionation (or three if P^{1a} is orange instead of yellow):

Tantalum fraction: P^1 (main fraction), P^{1a}.
Intermediate (mixed) fraction: P^{1b}, P^{1c}.

The four precipitations are done in one day, filtration of P^{1c} taking place the next morning.

P^1 (*yellow*): the gradual addition of tannin is continued while the boiling liquid is being stirred; with high tantalum contents a yellow precipitate will be formed. Any orange coloration appearing at the point of incidence of the reagent is made to disappear by agitation. The addition of tannin is interrupted before any permanent colour-change takes place; in no case is more than 50 c.c. of tannin reagent added. Complete flocculation is brought about by addition of 30 to 50 c.c. of saturated ammonium chloride solution; partial neutralisation with N ammonia to induce precipitation is hardly ever necessary in the case of P^1. The solution is boiled gently for 5 to 10 minutes, and left on the water-bath for half an hour. The precipitate P^1 is collected, well washed (return to precipitation beaker), and ignited in crucible *p*.

P^{1a} (*yellow*): the filtrate from P^1 is boiled down while the precipitate is being washed; the total volume of filtrate and washings is kept approximately constant during each fractionation. The boiling solution is cautiously treated with N ammonia until a permanent cloudiness appears, then slowly titrated with tannin, being agitated meanwhile. The bulky P^1 having been eliminated, it is usually possible, by observation of the delicate colour changes, to obtain an additional yellow fraction P^{1a}. This is treated, as before, by boiling and digestion on the water-bath. If yellow, the washed P^{1a} is added to P^1. If, however, P^{1a} appears orange after settling on the water-bath, the gradual addition of N ammonia and tannin should be continued; this will produce a larger precipitate of decided orange colour, *i.e.* the first intermediate precipitate P^{1b}.

P^{1b} (*orange*): the concentrated filtrate from the yellow precipitate P^{1a} is boiled, stirred, treated with N ammonia until slightly cloudy, and titrated with tannin until a deep orange precipitate is produced. The ignited P^{1b} should amount to 0·01 to 0·02 grm. After boiling, digestion on the water-bath, and filtration, the washed precipitate is ignited in crucible *s*.

P^{1c} (*red*): the concentrated filtrate from P^{1b} is treated exactly as the preceding filtrate, but the red precipitate P^{1c}, after digestion on the water-bath, is set aside overnight before filtration. The washed P^{1c} is added to P^{1b}; the tantalum-free filtrate F^{1c} is concentrated in beaker B.

The precipitation of the intermediate fraction in two portions is always advisable, as total precipitation of the tantalum has not necessarily taken place when incipient precipitation of niobium becomes evident: at low tantalum and high niobium concentrations the two stages overlap. If P^{1b} is orange at first and reddens with continued addition of ammonia and tannin, whilst P^{1c} is decidedly reddish at the time of its formation, it may safely be inferred that total precipitation of tantalum has been achieved.

Each fraction is weighed to the nearest mgrm.; the colour and weight of the precipitates are recorded as important guides, together with the amount of tannin added.

(*b*) *The Coloration is Orange to Red.*—No tantalum fraction will be obtained. The mixed fraction, containing all the tantalum and some niobium, is produced in two portions, P^1 and P^{1a}, which correspond with P^{1b} and P^{1c} of the preceding case.

P^1 (*orange to red*): the addition of tannin to the boiling solution is regulated from a minimum of 10 c.c. (for low Ta : Nb ratios) to about 20 c.c. The precipitate is flocculated by addition of 30 c.c. of the ammonium chloride solution, if necessary a little N ammonia, boiling, and digestion on the water-bath. It is collected, washed, and ignited in crucible *s*.

P^{1a} (*red*): the concentrated, boiling filtrate from P^1 is treated with a little N ammonia, followed by tannin; a red precipitate should be obtained, yielding about 0·02 grm. of ignited oxide. The liquid is set aside overnight; P^{1a} is collected, washed, and added to P^1. The tantalum-free filtrate, F^{1a}, is concentrated in beaker *B*.

Second Fractionation.—The weighed intermediate fraction ($P^{1b} + P^{1c}$) (case *a*), or the mixed fraction ($P^1 + P^{1a}$) (case *b*), is fused with bisulphate, and the product dissolved in ammonium oxalate solution.

The second fractionation is exactly like the first. The operations take place on a reduced scale; the manipulative details remain identical. The boiling oxalate solution is cautiously titrated with tannin, which produces either a yellow (*c*) or, if the tantalum content is very low, an orange to red (*d*), coloration.

(*c*) *Yellow Coloration.*—Properly performed, the first fractionation of a tantalum-rich mixture gives a small intermediate fraction ($P^{1b} + P^{1c}$), the niobium-content of which is sufficiently low (see example *A* below) to enable the operator to complete the separation at this stage. The directions will be found under "*Final fractionation.*"

If, on the other hand, the original oxide mixture contained substantial quantities of both oxides, then the intermediate fraction will be heavier (example *c*), and its re-treatment will constitute the penultimate fractionation. Three precipitations are carried out (four are hardly necessary):

P^2: yellow. Ta fraction; to crucible *p*.
P^{2a}: yellow or orange (see below).
P^{2b}: orange to red. Mixed fraction; to crucible *s*.

The precipitate P^{2a} is disposed of according to its colour: if yellow, it is added to P^2; if orange, to P^{2b}. It is not at all uncommon to obtain a yellow P^{2a}. The tantalum-free filtrate F^{2b} is added to beaker *B*.

(*d*) ORANGE TO RED COLORATION (very low tantalum content).—Another mixed fraction, in two portions, will have to be produced, exactly as in the first fractionation (case *b*):

P^2: orange to red. To crucible *s*.

P^{2a}: red. Collected next day; to crucible *s*.

The tantalum-free filtrate F^{2a} is added to beaker *B*. In the present case, ($P^2 + P^{2a}$) should not be subjected to final fractionation without an intervening third fractionation, which must yield a yellow head-fraction P^3.

FINAL FRACTIONATION.—As explained under *Rationale*, the final tantalum fraction to be produced should be slightly niobiferous; hence the mixed fraction submitted to final fractionation should be as small as possible, and comparatively low in niobium. When to undertake the final fractionation is a matter for the operator's judgment, which must be based on each occasion on the colour as much as on the weight of the intermediate fraction to be treated. The examples given in the Experimental Part are perhaps the best practical guide for this part of the process.

The intermediate fraction having been dissolved as before, the boiling solution (50 to 100 c.c.) is treated with tannin until a pale orange coloration is obtained. Flocculation is induced by 10 to 20 c.c. of ammonium chloride solution and a few drops of *N* ammonia. Should the coloration be yellow, the final fraction can be obtained in two portions, a yellow precipitate first, and a pale orange one in the filtrate therefrom.

DETERMINATION OF THE TANTALUM.—The weight of the tantalum fraction must always be corrected for adsorbed salts, silica (filter ash), and probably titania. The combined ignited precipitates are lixiviated with 2 per cent. hydrochloric acid, collected, strongly ignited, and weighed. The oxide is then fused with bisulphate, the product is dissolved in ammonium oxalate, and the slight residue is collected, washed, ignited, and weighed as SiO_2. The cold oxalate filtrate is treated with dilute sulphuric acid and hydrogen peroxide, and the titania, if any, is determined colorimetrically. The sum of SiO_2 and TiO_2, subtracted from the weight of the leached precipitate, gives the net weight of Ta_2O_5.

DETERMINATION OF THE NIOBIUM.—This oxide may be taken by difference. For a direct determination, the combined niobium filtrates are boiled with 0·5 to 1 grm. of tannin and a small excess of ammonia. The ignited (generally ferruginous) precipitate is fused with bisulphate, the mass is dissolved in ammonium oxalate, and the solution is freed from silica by filtration; the filtrate is neutralised with *N* ammonia and diluted with an equal volume of saturated ammonium chloride solution, and the niobium is precipitated with tannin, as directed in Section XIX, D (*loc. cit.*). The ignited precipitate is leached, weighed, and tested for titania like the tantalum precipitate.

EXPERIMENTAL

Four examples of the application of the process are given. The composition of the mixed oxides treated is represented by the following $Ta_2O_5 : Nb_2O_5$ ratios:— 4:1 (*A*); 1:4 (*B*); 3:2 (*C*); and 1:300 (*D*).

Example A.—Taken: 0·2023 grm. of Ta_2O_5, 0·0550 grm. of Nb_2O_5.

Tannin solution c.c.	Fractionations		Gross weight of precipitates	
	First	Second	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
50	P^1, yellow			0·1866
20	P^{1a}, yellow			0·0144
5	P^{1b}, orange	re-treated	0·0070	
5	P^{1c}, red		0·0040	
18		P^2, yellow		0·0042
3		P^{2a}, pale orange		0·0008
			Gross weight of Ta_2O_5 fraction	0·2060
			Less leaching loss 0·0030 grm., SiO_2 0·0012 grm.	0·0042
			Net Ta_2O_5 found	0·2018

Mixtures rich in Ta_2O_5 provide the simplest case for separation. More than 90 per cent. of the Ta_2O_5 is recoverable as P^1.

Example B.—Taken: **0·0516 grm.** of Ta_2O_5, **0·2006 grm.** of Nb_2O_5, **0·0012 grm.** of TiO_2.

Tannin solution c.c.	Fractionations			Gross weight of precipitates	
	First	Second	Third	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
20	P^1, orange	re-treated		0·0624	
5	P^{1a}, red			0·0160	
10		P^2, yellow			0·0422
3		P^{2a} (see below)	re-treated	0·0140	
1		P^{2b} reddish		0·0144	
5			P^3, yellow		0·0114
1			P^{3a}, pale orange		0·0034
				Gross weight of Ta_2O_5 fraction	0·0570
				Less leaching loss 0·0016 grm., SiO_2 0·0027 grm., TiO_2 0·0009 grm.	0·0052
				Net Ta_2O_5 found	0·0518

The separation was satisfactory, although the Ta_2O_5 : TiO_2 ratio of 43 is rather low (*cf.* Section XI, ANALYST, 1928, 53, 266). We were over-cautious in our earlier paper when we stated that the titania should "not much exceed 1 per cent. of the tantalic oxide to be determined"; it appears from this test that 2 per cent. does no harm.

The appearance of P^{2a} was rather deceptive: it was intended to be added to P^2, but, when packed on the filter (which is always the safest way to judge of the colour of the precipitates), it appeared too impure for a tantalum fraction; hence it was re-treated. As will be shown in a subsequent paper, tungsten acts like titanium in affecting the colour of the tantalum precipitate.

Example C.—Analysis of a pure preparation of mixed pentoxides used in test analyses (Section VIII, ANALYST, 1927, **52**, 512). Taken: 0·3300 grm.

Fractionations			Weight of precipitates	
First	Second	Third	Mixed fractions Grm.	Ta_2O_5 fractions Grm.
P^1, yellow				0·1759
P^{1a}, orange P^{1b}, red	re-treated		0·0537	
	P^2, yellow			0·0208
	P^{2a}, yellow			0·0027
	P^{2b}, orange	re-treated	0·0072	
		P^3, yellow		0·0016
		P^{3a}, pale orange		0·0015
			Net weight of Ta_2O_5 fraction	0·2025

Ta_2O_5, 61·4 per cent.; Nb_2O_5 (by difference), 38·6 per cent.

In this older analysis the amount of tannin used was not recorded. The net weights of the tantalum precipitates are given; P^1 was purified by itself by the usual lixiviation process. The figures for the other four tantalum fractions represent the weight less filter-ash.

Example D.—Analysis of a preparation of niobic oxide:—Taken: Two 1-grm. portions, fractionated as in Section V (ANALYST, 1925, **50**, 496). Five successive treatments.

Tannin solution c.c. per portion	Fractions		Grm.
10	P^1 (red), combined, from two portions		0·565
10	P^2 (red)		0·122
5	P^3 (orange) 0·0250; P^{3a} (red) 0·0110.	ΣP^3	0·0360
5	P^4 (pale orange) 0·0066; P^{4a} (orange) 0·0056.	ΣP^4	0·0122
4	P^5 (yellow) 0·0045; P^{5a} (pale orange) 0·0029.	ΣP^5	0·0074

The net weight of the Ta_2O_5 fraction is 0·0074 grm., the impurities having been filtered off after solution of the bisulphate melt of ΣP^4 in ammonium oxalate. Hence the Ta_2O_5 content of the preparation is 0·37 per cent. Mr. A. R. Powell, having worked quite independently, and in ignorance of my result, reported 0·32 per cent. of Ta_2O_5 in the material.

It only remains to be added that the coloration of the tannin filtrates is of no diagnostic importance in the fractionation: in fact, it will be found that the filtrates obtained by the application of the revised procedure are colourless, or nearly so. I am now satisfied that the straw-yellow colour discussed in the earlier paper was caused by excess of tannin. An orange or reddish filtrate indicates incomplete flocculation, which is easily corrected by addition of more ammonia or tannin. Ammonium oxalate solution, applied in the earlier work as a means for depressing the hydrogen ion concentration, has proved to be unnecessary, and its use has been discontinued.

SUMMARY.—An improved procedure for the separation of tantalum from niobium, based on fractional precipitation of the oxalate solution by tannin, is described. Four instances of the application of the method to mixtures of the two oxides in various proportions are recorded.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
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An Improved Micro-Apparatus for the Determination of Molecular Weight

BY A. F. COLSON, B.Sc., A.I.C.

(Read at the Meeting of the North of England Section, October 15, 1932)

WHEN using the macro-apparatus devised by Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314) for the determination of molecular weight by the ebullioscopic method, it is necessary to fulfil the following conditions in order to obtain reliable results:—(1) The upper bulb of the differential thermometer must be adequately bathed by the condensed solvent. (2) The apparatus (including the flame used to boil the solvent) must be properly shielded from air-draughts. (3) The volume of the solvent at its boiling-point must be determined in such a manner that no appreciable drainage of condensate from the inner walls of the apparatus can take place before the required reading of the volume is made.

The first of these conditions is satisfied to a certain extent in the macro-apparatus in the following manner:—Two short wires are attached to the differential thermometer at a point above the upper bulb. When the thermometer is in use these wires make contact with the inner wall of the condenser, and serve to direct a stream of condensed solvent towards the neighbouring bulb of the thermometer.

To fulfil the second condition to some extent, the apparatus is provided with a loosely-fitting glass cylinder. This cylinder is inside the apparatus and acts as a screen to the thermometer.

The third condition is the most difficult one to satisfy. An accurate determination of the volume of the solvent at its boiling-point cannot be made by removing the flame from under the boiling vessel, and reading off the volume as soon as the surface of the liquid has become sufficiently quiescent. This method fails because the heat retained by the vessel containing the solvent is sufficient to keep the liquid feebly boiling for two or three seconds after the flame has been removed. During this short period sufficient condensed solvent drains down from the walls of the apparatus to make an accurate reading impossible.

Menzies and Wright (*loc. cit.*) determined the volume by removing the flame and cooling the solvent in a beaker of cold water immediately before taking the reading.

If these three operations are carried out in the shortest possible time a fairly satisfactory determination of the volume can be made, but the method is undoubtedly inefficient and leaves much room for improvement.

The efficiency of the micro-apparatus recently devised by Milner and Smith (*Mikrochemie*, 1931, 3, 117) is similarly impaired by this imperfection in the method of measuring the volume of the solvent.

By the adoption of an entirely different method of heating the solvent it has been found possible to construct an apparatus which is free from the defect common to the macro- and micro- forms referred to above. This improved micro-apparatus is described below.

The solvent is heated electrically. A spiral of thin platinum wire, wound on a core of glass rod, about 1 mm. in diameter, constitutes the heating element, A, which is immersed in the solvent. The ends of the coil are joined to two platinum leads which are sealed through the walls of the vessel V and carry the terminals B^1 B^2. The resistance of the spiral is about 3·0 ohms, and the current required to heat the solvent sufficiently is about 2·8 amps.

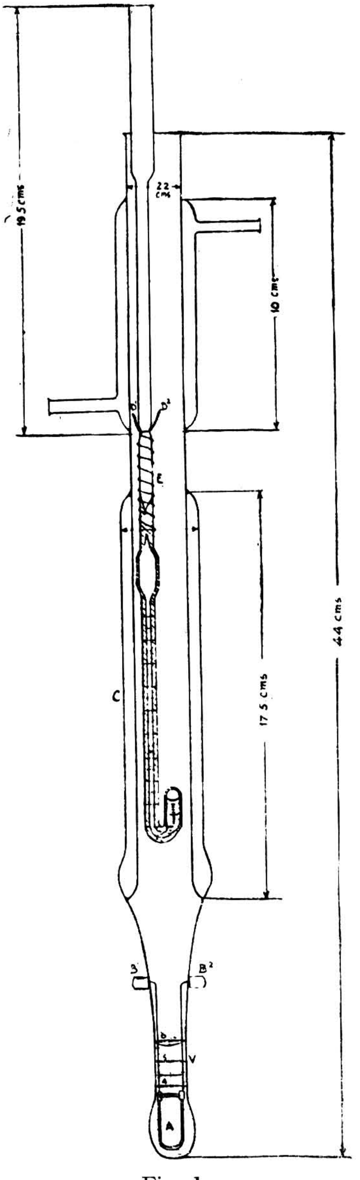


Fig. 1

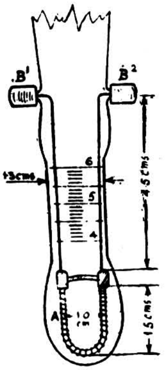


Fig. 2

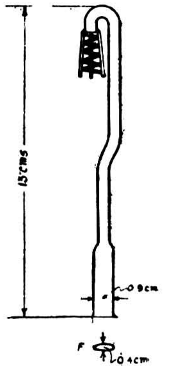


Fig. 3

The copper spiral E, used by Milner and Smith (*loc. cit.*), has been adopted because it produces a more efficient bathing of the upper bulb of the differential thermometer than is possible with the two wires D^1 D^2 alone. This spiral is joined to the junction of the wires D^1 D^2, and extends to the bulb of the thermometer.

The vacuum jacket, C, which is also a feature of Milner's and Smith's apparatus, affords better protection from air-draughts than the internal vapour jacket formerly employed. The Cottrell pump, F, has been very slightly modified, as shown in Fig. 3, in order that the lower end may pass easily between the platinum leads in the vessel V.

Since the apparatus is a modification of the macro-form devised by Menzies and Wright (*loc. cit.*), the method of making a determination of molecular weight is essentially the same as that given in their paper.

A few special points peculiar to the improved micro-apparatus must be mentioned.

To determine the volume of the solvent at its boiling-point the current is stopped, and the required reading is taken at once. The solvent becomes quiescent and in a suitable condition for measurement so soon after the current is stopped that the cooling, which is necessary in all the types of apparatus hitherto used, is not necessary in this improved apparatus. A number of measurements can be made very easily and quickly, the agreement between them being of the order of 0·02 ml. The substance of which the molecular weight is required is introduced into the solvent in a glass cup, 0·4 cm. in diameter and 0·4 cm. deep.

The volume of solvent used should not be more than about 6 ml. Two further advantages afforded by the use of the apparatus here described are:—(1) The source of heat is not susceptible to air-draughts. (2) The height to which the solvent rises in the condenser—and consequently the volume of solvent remaining in the boiling vessel—can be fixed by keeping the current constant.

In order that the readings registered by the differential thermometer shall remain steady during a determination, it is important to ensure that the wires D^1 D^2 make contact with the inner wall of the condenser at points not appreciably less than 1 cm. below the upper edge of the column of condensed solvent.

The table below shows some results obtained with coumarin (mol. wt.=146) in benzene as solvent.

Weight of coumarin Mgrms.	Volume of benzene Ml.	Boiling-point of benzene °C.	Rise above zero reading Mm.	Conversion factor	Ebullioscopic constant	Molecular weight
10·599	5·05	80·8	9·4	0·004833	32·0	148
8·369	5·23	80·5	6·9	0·004884	,,	150
15·647	5·23	,,	13·7	,,	,,	143
5·921	5·70	80·2	4·6	0·004935	,,	147
13·459	5·70	,,	10·3	,,	,,	149

I wish to thank the Directors of Imperial Chemical Industries, Limited, for permission to publish the results of this work.

Sediments in Ink and in Writing

BY C. AINSWORTH MITCHELL, D.Sc., F.I.C., AND T. J. WARD

(*Read at the Meeting, May* 4, 1932)

FOR several years we have been studying, more or less independently, the nature of the sediments which form in ink and their significance in writing.

NORMAL SEDIMENTATION IN INK VATS.—All inks made from galls, copperas, dye, and acid are allowed to stand for several weeks at least, in order that the vegetable débris and the more insoluble iron-tannin compounds may subside. The sludge at the bottom of the vat varies in composition, but usually contains a considerable proportion of the blue dyestuff, which has been carried down mechanically, and, when oxalic or tartaric acid has been used as the stabilising agent, it will also contain insoluble oxalates or tartrates. The amount of iron in the dry deposit has been found to range from less than 5 per cent. to over 27 per cent., as is shown by the following partial analyses of actual deposits, dried at 100° C.

	I Per Cent.	II Per Cent.	III Per Cent.	IV Per Cent.	V Per Cent.
Mineral matter	17·51	49·04	9·12	10·12	14·20
Organic matter	82·49	50·96	90·88	89·88	85·80
Iron in deposit	13·12	27·35	6·28	4·76	7·06
Iron in mineral matter	74·92	55·77	68·85	45·68	49·71

Special interest attaches to No. V, since it is a deposit from a vat of gallic acid ink. In one experiment, on a large scale, in which the sediment was separated by centrifuging, the moist solid material contained 0·38 per cent. of the blue dye.

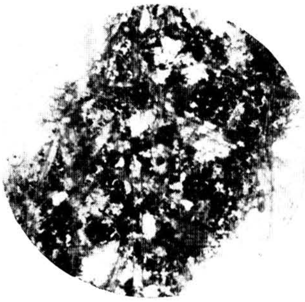
If the ink is drawn off before sedimentation is complete, the process will continue in the bottle, and eventually a very fine deposit will be thrown down and will spoil the appearance of the ink. Writing done with ink containing such deposit will differ in appearance under the microscope from that done with a normal clear ink, as may be seen in Pl. I, 1 and 9.

ABNORMAL SEDIMENTATION.—If the proportion of iron to the tannin has not been correctly calculated to yield a soluble iron tannate which will oxidise but slowly, an insoluble iron tannate will be rapidly formed, and, except for the iron gallate present, the ink will be decolorised.

For example, in experiments in which that remarkable glucose-free gallotannin, previously described (ANALYST, 1923, **48**, 7, 328), was used, the following typical results *inter alia* were obtained. For practical purposes the 10·1 per cent. of gallic acid in this tannin may be ignored, since it has little effect upon the calculations.

Gallotannin Grm.	Iron sulphate Grm.	Ratio of tannin to iron	Effect
0·1	0·1	10 : 2	Precipitation in 5 days
0·1	0·05	10 : 1	Precipitation in 10 to 15 days
0·1	0·025	10 : 0·5	Stable for six weeks

PLATE I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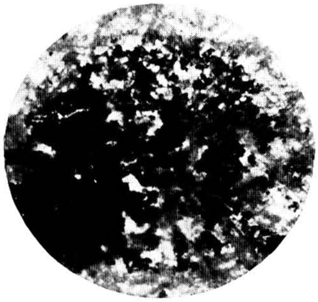
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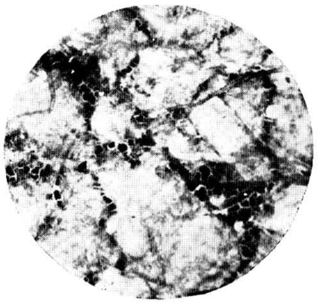
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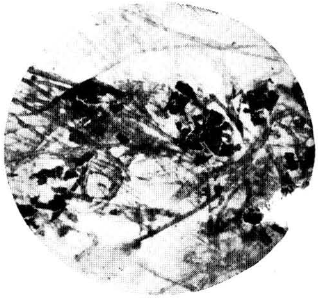
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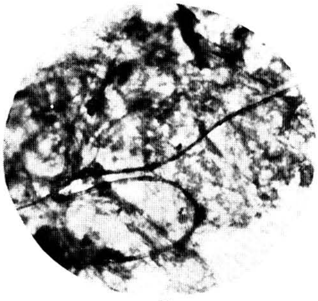
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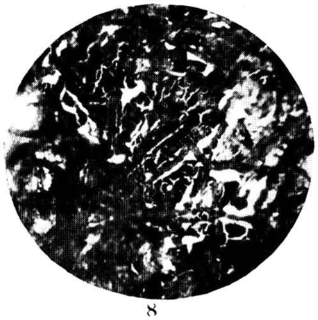
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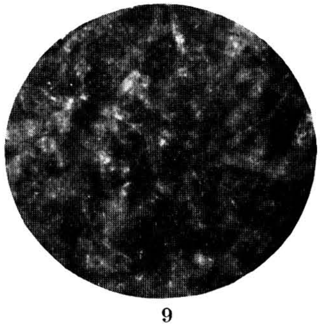
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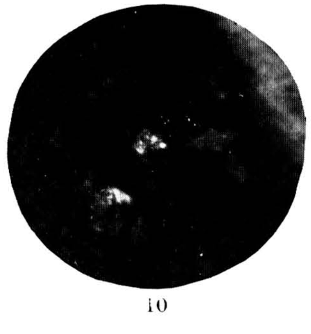
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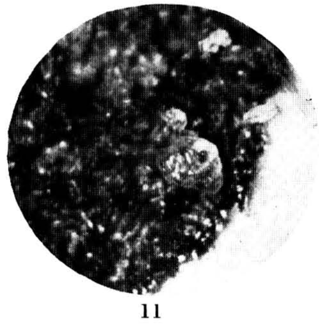
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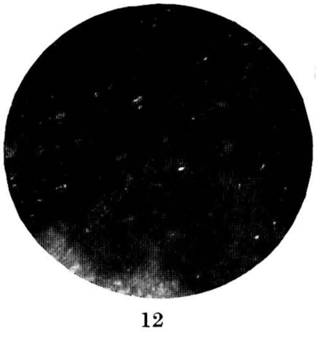
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(1) Normal sediment.
(2) Excess of tannin.
(3) Excess of iron.
(4) Excess of gallic acid.
(5) Frozen ink.
(6) Effect of pen left in ink.
(7) Mould hyphae.
(8) Effect of alkaline glass.
(9) Oxalic acid sediment in vat.
(10) Sand in letter, 1842.
(11) Sand in book, 1840.
(12) Pumice in letter, 1837.

PLATE II

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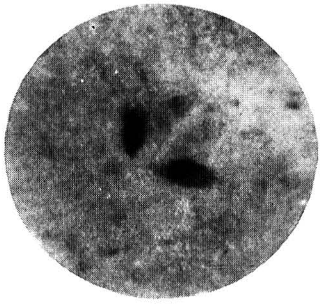

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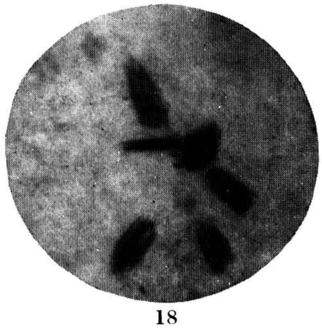

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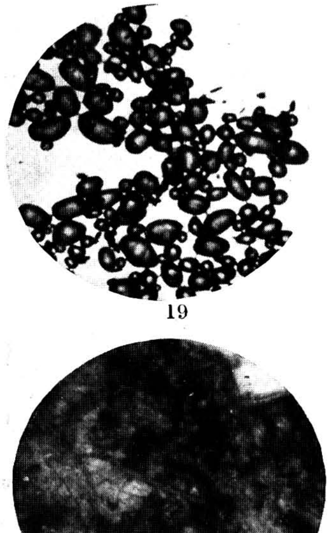

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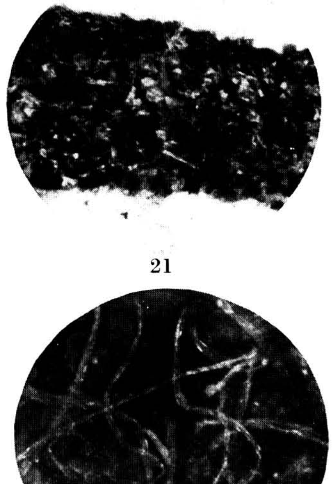

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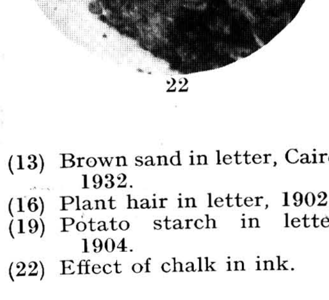

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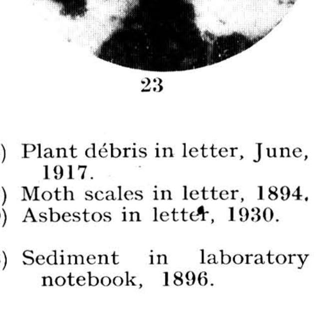

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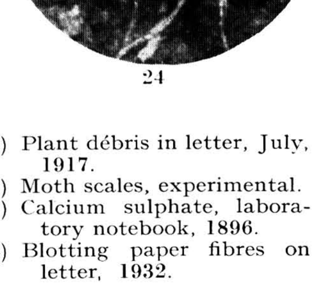

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(13) Brown sand in letter, Cairo, 1932.

(14) Plant débris in letter, June, 1917.

(15) Plant débris in letter, July, 1917.

(16) Plant hair in letter, 1902.

(17) Moth scales in letter, 1894.

(18) Moth scales, experimental.

(19) Potato starch in letter, 1904.

(20) Asbestos in letter, 1930.

(21) Calcium sulphate, laboratory notebook, 1896.

(22) Effect of chalk in ink.

(23) Sediment in laboratory notebook, 1896.

(24) Blotting paper fibres on letter, 1932.

Hence, the ratio of iron to tannin should be about 5:100, and if there is much deviation from this proportion in either direction, precipitation may occur either in the vat or, later, in the ink-bottle.

The effect of excess of either ingredient in the ink may appear in writing done with it. If there is excess of iron, the ink will stain the paper in a uniform bluish-green layer (Pl. I, 3), in which the usual large masses of black pigment will not appear, whereas if there is an abnormal excess of tannin the accumulations of pigment will appear as large black irregular clots (Pl. I, 2).

SEPARATION OF GALLIC ACID.—Occasionally, a crystalline film may form on the surface of the ink in a closed bottle and lead to complaints which will puzzle an ink-maker, since he is confident that no change has been made in the formula used in the preparation of an ink which has previously proved satisfactory. The explanation of the trouble depends upon the fact that the solubility of gallic acid is so small that an ink, especially one prepared from tannic acid (gallotannin), may become saturated with gallic acid at a relatively high temperature, and if the bottle is then exposed to a somewhat lower temperature, the gallic acid will separate in minute crystals on the surface.

Solubility of Gallic Acid.—The following table shows the solubility of pure gallic acid (dried at 100° C.) in distilled water at various temperatures. The gallic acid used contained 10·3 per cent. of water, and its purity, determined colorimetrically by comparison with pyrogallol (ANALYST, 1923, **48**, 2), was 100 per cent. (m.pt., 241° C.). When this gallic acid was heated with boiling water until a homogeneous liquid was obtained, the solution contained 48·71 per cent. (by weight) of gallic acid. At other temperatures the percentage solubility (w/w) was as follows:

Temperature	43°C.	32°C.	28°C.	21°C.	15°C.	7·5°C.	5·5°C.	5·0°C.	3°C.
Solubility	3·39	2·61	2·17	1·72	0·91	0·76	0·74	0·73	0·59

Commercial Gallotannins.—The following analyses, which are typical, are those of two commercial gallotannins, the first of which produced a crystalline film on the ink made from it, whilst the other did not. The tannin and gallic acid were determined by the colorimetric method (*loc. cit.*).

	A Per Cent.	B Per Cent.
Water	9·9	6·2
Total tinctogenic value (in terms of gallic acid)	[64·8 per cent.]	[62·0 per cent.]
Gallic acid	39·7	12·4
Gallotannin	25·1	49·6
Non-tinctogenic substances	25·3	31·8

The consignment A contained an exceptionally high proportion of gallic acid, with the result that the ink must have reached its saturation point for that acid at the ordinary temperature (15·5° C.), and, when chilled, readily produced a crystalline film.

The appearance of writing in ink from which the gallic acid has crystallised is characteristic. (Pl. I, 4.)

FROZEN INK.—A condition under which an ordinary blue-black ink might appear to be a mixture of a writing- and a copying-ink is when it has been frozen and is in the state of thawing. One would hardly anticipate that anyone would be so unreasonable as to write with a half-thawed ink and then to complain of the result, and yet on several occasions ink-manufacturers have had to investigate such complaints.

If an ordinary iron-gall blue-black ink is frozen into a solid disc, a fractionation occurs. The edges of the mass are colourless, whilst the iron tannate and dye become concentrated in the middle and lower parts of the disc. When the part which thaws first beneath the mass is decanted it will be found to contain approximately twice as much blue dye as the original ink, whilst the iron tannate and other constituents will show a corresponding increase. With a gallic acid ink the separation into fractions is much less pronounced than with an iron-gall ink. The following figures give some idea of the fractionation that occurs.

FROZEN INKS

	Original ink Per Cent.	Part first thawing Per Cent.	Residue thawing last Per Cent.
Iron-gall ink.			
Total solids	3·60	6·39	1·19
Mineral matter	0·56	0·82	0·24
Iron	0·28	0·47	0·16
Gallic acid ink.			
Total solids	3·34	4·24	2·16
Mineral matter	0·38	0·66	0·30
Iron	0·28	0·41	0·14

If a partly-thawed ink is used for writing, the portion near the bottom of the ink-bottle will produce the effect of a copying-ink, that is to say, will show an increased deposit of blue and black pigments, and may appear iridescent in places. It may also appear to contain spicules (Pl. I, 5), although, in reality, these are cavities from which the ice-crystals have melted. On the other hand, the upper part will be deficient in dye and iron tannate, and will produce paler writing than the bottom fraction.

EFFECT OF PEN LEFT IN INK.—One of the most frequent causes of the decomposition of ink in ink-wells is the practice of leaving the pen in the ink. The acid in the ink soon dissolves the iron of the nib, and when an excess of iron in proportion to the tannin is reached, an insoluble tannate is precipitated.

Many years ago one of us based a crude test for the acidity of inks on the determination of the loss in weight by a pen-nib immersed in the ink, and the method was subsequently officially adopted (without acknowledgment) in the United States. The test is still a useful one for comparative purposes, as is shown by the following results recently obtained by leaving weighed pen-nibs for 20 days in 10 c.c. of different inks, and subsequently cleaning, drying, and weighing the nibs.

	Loss in weight of nib	Original ink			Filtrate from deposit		
		Total solids	Mineral matter	Iron	Total solids	Mineral matter	Iron
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
A. English ink	10·99	3·25	0·42	0·20	2·27	0·8	0·46
B. Ditto	12·05	4·00	0·84	0·35	2·17	1·05	0·76
C. Japanese ink	12·75	5·28	2·02	0·59	3·83	2·47	0·80

Writing done with ink which has been decomposed by a pen-nib appears, in a photomicrograph, very similar to that done with an ink containing an excess of copperas. (Pl. I, 6.)

WATERED INK.—Another common cause of sediments in ink is the practice, sometimes adopted in cottages, of eking out the ink by the addition of water. Frequently the deposit in an ink-well has become largely insoluble, and the addition of water not only reduces the colour of the soluble dye, but also leaves particles of sediment. The effect of such dilution on writing is usually quite distinct from that of a blotted ink, which will generally show a pale uniform ground, without the solid particles to be seen in watered ink.

DEPOSITS IN MIXED INKS.—The admixture of two inks of different character may cause sediments to form, and these may be conveyed into the writing. This was the explanation of the abnormalities in the case of *Skelton* v. *Hawes*, in which a will had been written in a mixture of three different inks, and the strokes of the writing showed not only particles of sediment, but also different colours in different parts of the signatures (see ANALYST, **1932**, 146).

Attempts to age an ink artificially may also sometimes be detected by an examination of the writing, as happened in a case in which a clerk had falsified a ledger by writing up the entries in a mixture of ordinary ink and Indian ink. The addition of a drop of dilute sodium hypochlorite to one of the characters at once revealed the fraud, for the particles of lamp-black derived from the Indian ink remained unbleached.

Accidental dipping of the pen into the wrong bottle of ink may afford useful evidence in the writing. An instance of this occurred in the case of *Rex* v. *Thurburn*, in which the defendant was charged with writing anonymous letters. An admitted document in the case was a series of caricatures drawn in artist's black ink, and the fact that two of the printed characters in the middle of the writing on an anonymous card were in the same kind of ink indicated that the writer of that card had accidentally dipped the pen into a bottle of that ink.

In a more recent case (*Riddle and Holder* v. *Midland Bank*, 1932) there were on a document two signatures, the authenticity of which was not disputed, although there was a sharp conflict of evidence as to the place where they were signed, the plaintiffs contending that they were signed separately in Banbury, and the defendants that they were signed at the same time in a bank manager's office. The upper signature was written in an ordinary blue-black ink, whilst in the other the dye of the ink formed a pale greyish-violet ground on which the black pigment was distributed in irregular spots. The microscopical appearance was consistent with that of an ink in which the blue dye had faded and the black pigment had formed a sediment in the ink-well (Fig. 25). This agreed with the story of the plaintiffs that the second signature had been signed with an old fountain-pen upon the nib of which the ink was encrusted, and that this had been dipped into a dirty ink-pot at a farm-house.

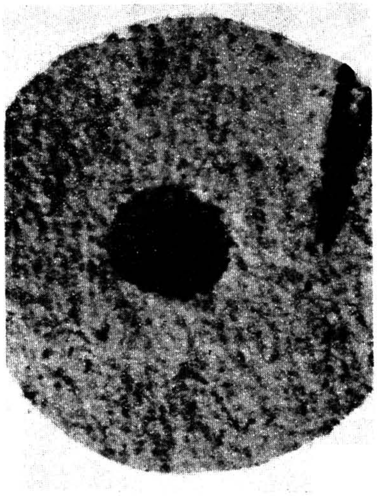

Fig. 25

Full-stop in signature, showing black deposit on grey back-ground × 50

The defendants accounted for the abnormal appearance of the second signature by the hypothesis that the pen had been accidentally dipped into a bottle of copying-ink standing open on the desk in the bank manager's office. Experiments, however, showed that the writing had none of the characteristics of a mixture of copying-ink and ordinary blue-black ink. These mix well and do not form a sediment, but the writing shows an increase of lustre due to the larger amount of aniline dye in the copying-ink. The signature in question, so far from showing an increase in dye, contained very much less than writing done with an ordinary blue-black ink.

EFFECT OF ALKALINE GLASS.—It has already been demonstrated (ANALYST, **1921**, **46**, 129) that ink may be completely decomposed by alkali dissolved from badly-made glass ink-bottles, and the appearance of writing in such ink is quite characteristic (Pl. I, 8), and not to be confused with writing in other forms of decomposed ink.

MOULDS IN INK.—In former times bay-salt was added to ink to prevent it from becoming hoary,* *i.e.* turning grey, through the growth of mould. In modern inks carbolic acid (or, less frequently, salicylic acid) is used for the same purpose. This precaution, however, is not always effective, for, occasionally, the ink in bottles which had been closed with a cork infected with mould will develop a growth which will eventually cause the ink to decompose, and infection with mould may also occur in ink exposed to the air in an ink-well.

This growth is not surprising, for, among the results recorded by Thom (*The Penicillia*, p. 90) are those of Sabalitscha and Dietrich (*Disinfektion*, **1926**, II, 67), who found that it required 0·14 per cent. of salicylic acid and 0·014 per cent. of phenol or thymol to inhibit the growth of a strain termed *Penicillium glaucum*. The optimum temperature for the growth of most species of *Penicillia* lies between 22° and 30° C. (Thom, *loc. cit.*, p. 85). Among the enzymes recorded as occurring

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* Harr = Anglo-Saxon, *grey*,

in *Penicillia* sp. are amylase, cytase, diastase, maltase, lactase, and emulsin. Our experiments show that oxydase may be added to these, for the addition of a trace of mycelium powder from a strain of *Penicillium** caused a pronounced acceleration in the precipitation of iron tannate from a solution of gallotannin and ferrous sulphate. This is shown by the following results, which are typical of many:

	Tannin Grm.	Iron sulphate Grm.		Time of standing Days	Precipitate Grm.	Iron in precipitate Per Cent.
(*a*)	0·1	0·1	blank	3	0·049	6·7
(*b*)	0·1	0·1	inoculated	3	0·082	5·38
(*a*)	0·1	0·1	blank	8	0·071	13·6
(*b*)	0·1	0·1	inoculated	8	0·091	13·2
(*a*)	0·5	1·0	blank	11	0·2884	8·45
(*b*)	0·5	1·0	inoculated	11	0·3550	—
(*a*)	0·1	0·05	blank	18	0·045	5·6
(*b*)	0·1	0·05	inoculated	18	0·090	12·9
(*c*)	0·1	0·05	inoculated	16	0·097	—
(*a*)	0·1	0·025	blank	35	nil	—
(*b*)	0·1	0·025	inoculated	35	0·0264	6·09

Hence, in each instance, the precipitation of gallotannin by the iron was greatly accelerated by the presence of the mould, and in some of the tests it was practically complete (for the 10 per cent. of gallic acid in the tannin remained in solution in each set of tests), whilst only 50 to 60 per cent. had been precipitated in the absence of mould. Further work on this method of measuring oxidising activity is in progress.

A proof of the fairly common occurrence of moulds in the inks of some twenty-five to thirty years ago is afforded by the fact that fragments of hyphae and mould spores may be looked for and found in the inks on old letters (see Pl. I, 7).

POUNCES IN WRITING.—Long after the invention of blotting-paper the practice of using sand or other powder to dry writing was continued, and indeed is not altogether obsolete at the present day. Originally, the term "pounce" (*poncer*) was applied to a powder which was dusted on to parchment to make it take the writing. The so-called cuttle-fish "bone" (or "scuttle-bone") was commonly used for the purpose (cf. *The Purefoy Letters*,† p. 288), and subsequently the term was applied to the powders used to dry the writing. We are indebted to Mr. A. Lucas for a specimen of an Egyptian account book of 1767, the ink on which he described in a paper read before the Society (ANALYST, 1922, **47**, 11). For drying this ink a mica powder had been used, and the deposit on

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* The *Penicillium* used in these experiments was kindly identified for us by Mr. Charles Thom, mycologist to the U.S.A. Department of Agriculture, as *P. terrestre, Jensen*, the name assigned to a group of strains rather than to a particular organism.

† *The Purefoy Letters*, 1735–1753. Edited by George Eland. 2 vols., with 28 plates. London: Sidgwick & Jackson, Ltd. Price 42s.

the strokes is particularly apparent in certain additional notes on the page (see Fig. 26).

Fig. 26
Mica crystals on writing in Arabic account-book of 1767 × 25

Blotting-paper has now to a large extent replaced sand as the drying agent in the Courts of Cairo, but Mr. Lucas has kindly sent us a specimen of a brown sand still used for this purpose by an aged writer claiming to be 95 years old (Pl. II, 13).

Chemical analysis of this sand gave the following results:—Moisture, 0·08; sand, 57·38; insoluble organic matter, 9·52; chlorides (as sodium chloride), 32·49; soluble organic matter (by *diff.*), 0·53 per cent.

Microscopical examination and sedimentation* tests showed the material to consist of granite sand containing angular and rounded grains of quartz, orthoclase felspar, biotite mica, and magnetite (Fe_3O_4). The vegetable constituents included fragments of seed coats, stems, leaves, and hairs impregnated with sodium chloride. The small quantity of insect débris consisted of wing cases, legs and antennae, probably derived from small beetles.

Examination of specimens of iron-gall writing will also often reveal particles of the pounce still adhering to the surface. For example, very finely powdered pumice was detected in a letter written in 1837 (Pl. I, 11), and particles of sand were found in a letter dated 1842 (Pl. I, 10) and in a book of 1840 (Pl. I, 12). It is possible that the potato starch found in a letter of 1904 (Pl. II, 19) was derived from the use of farina for drying the writing.

Fibres of blotting-paper adhering to an ink may sometimes be distinctive, as is to be seen in the photomicrograph of the ink on an envelope received from Paris this year (Pl. II, 24).

EVIDENTIAL VALUE OF SEDIMENTS IN WRITING.—It is obvious that under certain conditions the presence of extraneous material contained in the ink may have some evidential value. For example, the fine asbestos fibres found in a letter written in 1930 from an engineer's office (Pl. II, 20) is suggestive of the origin of the letter. In another instance plant débris (probably straw dust, for it gave a ligno-cellulose reaction) was found in a letter of June, 1917, whilst similar particles were found in another letter written from the same house, but a month later (Pl. II, 14 and 15).

In a legal document a letter had been added to certain words, either by the original writer immediately after the writing was completed or fraudulently by

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* The principle adopted was that of the "gravity column," originally described by Sollas, in which a column of mixed liquids gradually increasing in density downwards is used. A narrow glass tube, about 80 cm. in length, was filled with a mixture of benzene and pure bromoform (commercial samples are frequently impure), the proportion of the latter increasing towards the bottom of the tube, thus giving a column of liquid ranging in sp.gr. from about 0·88 at the top to 2·90 at the lower end. The fragment of unknown material was dropped into the tube, and small glass bulbs or small (insoluble) crystals of inorganic salts of known sp.gr. were then added until one remained slightly above the fragment, and one just below it; the desired value was hen obtained by calculation.

another person on a subsequent date. Since it was not permissible to bleach the ink-strokes, which were in a heavy record ink and had not been blotted, search was made throughout the writing for thin portions in which sediment might be visible under the microscope. At seven points some sediment was detected. The added letters had been blotted, and the sediment also was easily visible. From the character and distribution of the various sediments it was highly probable that the added letters were written with ink from the same pot as used for the earlier writing. This conclusion was subsequently confirmed by other evidence.

DISTRIBUTION OF SEDIMENT IN WRITING.—The sediment transferred by the pen from the ink-pot to the paper may afford an indication of the stages in the course of the writing at which the pen was dipped into the ink. The strokes produced immediately after dipping sometimes contain the greater proportion of a heavy sediment, which diminishes (rapidly or slowly) in amount as the writing proceeds. Conversely, a light floating sediment, such as mould spores or insect débris, will occasionally increase in amount as the pen becomes depleted of ink.

METHODS FOR THE EXAMINATION OF DEPOSITS IN WRITING

For most specimens of writing a microscopical examination without any preliminary preparation is satisfactory. The writing may be examined as an opaque object by reflected light, by transmitted light if on translucent paper, or by a combination of the two methods. Owing to reflection from the glossy, and sometimes fluorescent, surface of many ink-strokes the modern methods of vertical illumination are seldom of value in the examination of ink sediments.

In some writings the normal ink-colour is in large amount, and almost obscures any sediment beneath. To overcome this absence of contrast and differentiate the sediment, the stroke may be partly bleached by spotting with $N/10$ hydrochloric acid, the excess of which is removed with filter-paper after a few seconds, and this treatment is repeated, if necessary. By this procedure the normal ink-colour is considerably lightened in tint, whilst the sediment is apparently unaffected, and may be readily observed and photographed.

IDENTIFICATION OF THE SEDIMENT OR DEPOSIT.—Sometimes the microscopic appearance of the sediment is in itself sufficient to enable one to determine its character, especially with organised structures such as plant and insect débris, textile fibres, etc. Other materials, however, may have to be removed from the writing, and the microscopic fragments submitted to a physical and chemical examination before their identity can be established. Of the various methods tried, we have found the following the most successful:

(*a*) *Sediments Soluble in Water.*—The ink-stroke is moistened with a minute drop of benzene, and gentle manipulation with a short, rigid, mounted needle will isolate the fragment, which is then dried and examined. The use of a rigid needle is emphasised, since a flexible one leads to much loss.

(*b*) *Sediments Relatively Insoluble in Water or Dilute Acid.*—The writing is brushed lightly with water or $N/10$ hydrochloric acid, and the fragments are collected in a camel-hair brush, which is then rinsed into water contained in a small centrifuge tube closed at the lower end with a rubber stopper. After being centrifuged the supernatant liquid is gently syphoned off, and, if necessary, the residue is washed with dilute hydrochloric acid and water in the tube to eliminate ink-colour. After the wash-water has been removed, the rubber stopper, bearing the residue on its end, is withdrawn. The separated particles are dried at a low temperature, and the specific gravity of one fragment is determined by means of a gravity column of mercuric iodide in potassium iodide solution, or of bromoform and benzene (*vide supra*). This is followed by microscopical examination to determine the crystallographic system, refractive index and angle of extinction in polarised light, after which suitable microchemical tests may be made. We have found it possible in some cases to identify a quantity of sediment not exceeding 0·05 mgrm. in weight.

PHOTOMICROGRAPHIC PROCEDURE.—Most of the photographs shown in the figures are magnified 50 diameters, this being obtained with an objective of 75 mm. focal length, and an eyepiece giving a magnification of 8 diameters. The specimens were illuminated as opaque objects with a bull's-eye condenser, and in some instances a little transmitted light was also used.

For documents from which small portions may be removed, illumination by means of the old-fashioned Lieberkühn reflector yields satisfactory results, and it has the advantages over vertical illuminators of being simpler to manipulate and of giving slightly angular illumination, which tends to eliminate confusing reflections from the surface of the ink.

Many colour filters were tried in order to reduce or eliminate the ink-colour and render the dark sediments prominent, and a diluted blue-black ink was found to yield good results in many cases. (*Cf.* Ward, ANALYST, 1930, **55**, 568.) The most generally useful filter for this purpose, however, was prepared by dissolving the ferric tannin compound (precipitated on keeping an ink without added dye for a long time) in fused phenol, and diluting the solution with water. With this filter the definition obtained is not particularly good, owing partly to the difficulty of focussing with the faint blue light available, and partly to the filter allowing some red light (in addition to blue and violet) to pass. To secure contrast when photographing extraneous deposits on the surface of the ink-strokes, a filter composed of a 10 mm. layer of a 0·35 per cent. aqueous solution of tartrazine was employed.

Most of the photomicrographs were taken on Wellington Anti-Screen plates, but, where the writing had become brownish in colour, Ilford Soft Gradation Panchromatic plates were used.

We wish to thank Mr. S. Creasey for his assistance in the analytical work.

DESCRIPTION OF THE PLATES

PLATE I

FIG.
1. Pen stroke with ink containing normal sediment × 50.
2. Pen stroke with ink containing excess of tannin × 50.
3. Excess of iron × 50.
4. Excess of gallic acid × 50.
5. Stroke made in ink, partly thawed × 50.
6. Effect of pen left in ink × 50.
7. Mould hyphae in ink-writing × 50.
8. Effect of alkaline glass on ink × 50.
9. Writing in ink containing oxalic acid in the sediment × 100.
10. Sand on writing in letter, 1842 × 50.
11. Sand on writing in book, 1840 × 50.
12. Pumice granules on writing in letter, 1837 × 100.

PLATE II

FIG.
13. Brown sand on writing in letter, Cairo, 1932 × 50.
14. Plant débris in ink-writing in letter, June, 1917 × 100.
15. Plant débris in ink-writing in letter, from the same house, July, 1917 × 100.
16. Plant hair in writing in letter, 1902 × 100.
17. Moth scales in writing in letter, 1894 × 50.
18. Moth scales (experimental) in ink-writing × 50.
19. Potato starch in ink-writing in letter, 1904 × 50.
20. Asbestos in ink-writing in letter from an engineer's house, 1930 × 100.
21. Calcium sulphate in ink-writing in laboratory notebook, 1896 × 25.
22. Effect of chalk in the ink × 50.
23. Sediment in ink in laboratory notebook, 1896 × 25.
24. Blotting-paper fibres on ink in letter from Paris, 1932 × 50.

DISCUSSION

The PRESIDENT, after commenting on the careful and remarkable manner in which this research had been presented, said that his own connection with ink was in rather a different category. He occasionally had to give an opinion as to the amount of sediment that an ink would give when in use, and he suggested that it might be possible to devise a method for determining this. He could very strongly support, as a good test for acid, the immersion of two or three clean, weighed nibs in the ink two or three days, and then wiping and re-weighing them. One could get very sound information, and, further, one was treating the actual material to be used in the ink. He had not realised, until Dr. Mitchell had mentioned the fact, that the subsequent addition to the American report was derived from Dr. Mitchell's suggestion.

Mr. R. F. INNES said that he was exceedingly interested in the paper, but from a different point of view than the authors had in mind. Could the authors say whether the oxidase in the mycelium of certain moulds would be able to act in the absence of iron. Presumably in the nib test the nib must be a steel nib. Was there any correlation between the corrosive action and the p_H of the ink?

Mr. E. R. BOLTON asked whether sodium fluoride had been tried to prevent the growth of moulds.

Mr. A. SCIVER expressed his appreciation of this very interesting paper. He, too, had been working on writing-inks for five or six months, and, although he did not wish to appear too much of an iconoclast, he had come to the conclusion that there was no really good ink on the British or American markets.

He asked whether the strokes in the first six slides were made with a brush or with a pen. With regard to the freezing of ink, he had recently been informed by a Japanese firm that the ink to be used by Russian and Japanese armies in Siberia had to resist intense cold, and that it would often freeze solid in the officers' fountain pens. Hence there must be some inks not affected by freezing. He, too, had intended to suggest the use of sodium fluoride as a preservative, but there were a number of efficient organic compounds available to-day.

With regard to the nib-corrosion test, he had found that practically all inks would produce a semi-solid crust if steel nibs were left in them. In his experience, the test had not proved successful, for, apart from the solution of the steel, he found it difficult to know when to stop rubbing the encrusted material from the nib after immersion in the ink. He asked whether any published figures were available of the p_H of inks now on the market. He had been unable to trace any direct connection between the p_H of an ink and the formation of sediment. It was difficult to devise a method that would give an indication of the weight of a sediment, but a simple volumetric method could be used. Had the authors tried the method of measuring the sediment in a long piece of tubing drawn out to a fine bore at one end?

In his opinion the development of sediment in ink required to be examined from the aspect of physical chemistry, and in particular from the aspect of colloid chemistry, as distinct from the ratio of the tannin and iron.

Dr. J. GRANT mentioned that papers of good quality were passed through a bath of very strong gelatin solution, and he wondered if this might affect the sediment in the ink used on the paper.

Mr. WARD, replying, said that in devising a standard method for determining the time of sedimentation it was necessary to take into consideration whether the ink was kept in a closed or an open bottle. If open, there were numerous factors which might influence the sedimentation.

With regard to the use of oxidation by moulds for the estimation of oxydase activity, it was quite possible that the presence of iron was not essential. Some two years ago Guthrie (ANALYST, 1930, **55**, 709) had estimated oxydase action by using the substrate formed by heating glucose with sodium hydroxide. The nib for the corrosion test should certainly be of steel, and not of stainless steel or gold. Different inks were stabilised with different acids—some with sulphuric, others with oxalic, and others, again, with acetic acid, and the degree of corrosion would vary with the acid. He had always found that brushing the nib with a tooth-brush in water was a satisfactory method of removing the incrustation.

Referring to the solidification of ink, Mr. Ward mentioned that he had seen an ink 75 per cent. of which became a solid jelly. It was contained in a cheap German fast-filling container of soda-glass. One had only to add a drop of water to the glass to obtain a distinctly alkaline solution.

The photomicrographs of the earlier slides all represented strokes made with a pen in the usual way. Referring to the photomicrograph showing the deposit of potato-starch in the writing, he mentioned that this deposit could be seen all through the letter, and was therefore obviously in the ink.

He did not agree with the observation of Mr. Sciver, that there was not a really good ink on the market; it depended upon the connotation of "really good." If one could buy an ink which would keep in good condition in the bottle for at least six months, he would consider that a satisfactory ink.

Dr. MITCHELL said that no definite relationship had been established between the p_H value and the corrosive action of different inks, although the determination of the hydrogen ion concentration was of comparative value. On the other hand, the method which he had devised of adding sodium acetate to an ink and distilling the liberated acetic acid (ANALYST, 1921, **46**, 131) had been found to afford a measure of the corrosive acid and acid compounds in an ink. Sodium fluoride would be an effective preservative against moulds, but would have the drawback of attacking the glass of the bottle. His remarks about the freezing of ink had been misunderstood: he had meant that it was unreasonable to complain of the results obtained with a half-thawed ink. A good ink should recover its original composition and properties after thawing. Physical methods of determining the stability of inks would probably prove of value, but in his experience the ratio of tannin to iron was as yet the best criterion. It was possible, as Dr. Grant had suggested, that the sizing material of the paper might affect the constituents of some inks. Mr. Sciver's volumetric method of measuring the sediment might sometimes be useful, but with many inks it would be difficult to determine the line of demarcation, owing to the dark colour of both ink and deposit.

Notes

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

THE ACIDITY OF GORGONZOLA AND STILTON CHEESES

IN 1922 some Stilton cheese came under notice because of a complaint of "a burning taste." The article had an acidity of 1·94 per cent., calculated as lactic acid.

In 1929 there was a further complaint, this time of a Gorgonzola cheese, alleged to have "a chemical taste," and it certainly had a sweetish acid taste, but not an unusual one for this type of article. It contained 1·60 per cent. of acid, calculated as lactic acid. Copper was present to the extent of one-fifteenth grain per pound.

As no other objectionable substance was found in either cheese, it seemed reasonable to attribute the taste in each instance to excess of lactic acid, provoking reactions in the tissues of mouths that may have been hyper-sensitive or sore through either inflammation or wounds, or because of food or drink taken previously.

Analyses of other samples of Gorgonzola cheese and one of Stilton (the twelfth in the table that follows), none of which appeared to be the subject of complaint, showed that, whilst amounts of 1·94 and 1·60 per cent. of lactic acid are above the average, they are not exceptional. But they do seem to indicate the zone of 1·6 to 1·9 per cent. of lactic acid to be that where occasional complaints may be expected, especially in articles in which the public has been educated by writers in popular weekly journals to expect copper salts.

The method for determination of acidity used was that given by Leach in *Food Inspection and Analysis*, Second Edition, 1909, p. 207, who cites as the source: *U.S. Dept. of Agric., Bureau of Chem. Bul.*, 46, p. 56. Reference to the latter shows the original source to be "Official Methods of Analysis adopted by the Association of Official Agricultural Chemists (U.S.A.)" of 1898.

Few references to the subject are to be found in chemical literature, but John Muter (ANALYST, 1885, **10**, 6) gives the average amount of water for Stilton cheese as 28·60 per cent., and the average acidity as 1·08. James Bell (*Chemistry of Foods*, 1883) gives for Stilton 23·57 per cent. of water and 1·24 per cent. of free acid (as lactic). Bell also gives figures for Gorgonzola cheese as 31·85 per cent. of water and 1·35 per cent. of free acid as lactic acid.

The data are arranged in order of the lactic acid content:

Number	Water Per Cent.	Acidity, as lactic acid Per Cent.	Number	Water Per Cent.	Acidity, as lactic acid Per Cent.
1	28·1	0·36	11	35·5	1·12
2	34·6	0·54	12	32·9	1·22
3	—	0·55	13	32·0	1·29
4	35·6	0·73	14	44·9	1·42
5	36·1	0·77	15	32·3	1·44
6	44·3	0·85	16	42·5	1·48
7	28·8	0·89	17	37·5	1·60
8	29·3	0·90	18	38·5	1·72
9	38·2	0·91	19	27·9	1·84
10	31·7	1·05	20	27·5	2·14

Comparison of the figures for water-content and acidity seems to show that there is no relation between them.

Three of the samples (Nos. 9, 16, and 6) contained fat in amounts (20·8, 28·0, and 28·9 per cent., respectively) substantially below that usual for Gorgonzola cheese.

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THE EXTRACTIVES OF RUM

IN *Aids to the Analysis of Food and Drugs*, Fourth Edition, 1918, there occurs the statement (p. 186) that rum contains from 0·7 to 1·5 per cent. of total solids. This being a datum that can be altered at the discretion of the manufacturer to suit the palates of purchasers, the matter is not of great importance, but the limits given were those stated by Pearmain and Moor in 1899, and do not appear to be characteristic. *Suggested Standards of Purity for Foods and Drugs* gives even higher figures in stating that "The extractive usually varies from 1·0 to 2·0 per cent." Church in *Food* (1882), p. 181, described a genuine sample of rum from the West Indies as containing "36½ grains of solid residue per pint." This corresponds with 0·42 per cent. w/v. Further, A. W. and M. W. Blyth, in *Foods: Their Composition and Analysis*, Sixth Edition (1909), p. 399, say: "As imported rum is a strong spirit containing 44 to 55 per cent. absolute alcohol, and from 0·3 per cent. to 1·0 per cent. extract, retailers mostly dilute it down nearer the legal limit of alcoholic strength."

The figures for the extracts given by forty-three samples of rum from various sources are tabulated below. The minimum was 0·30 and the maximum 1·13 grm. of total solids per 100 c.c. This shows fair agreement with the limits given by A. W. and M. W. Blyth. (Thirty-six of the samples were of the 30 U.P. type.)

Extract per 100 c.c. Grms.	Number of samples
0·30 to 0·40	11
0·41 to 0·50	7
0·51 to 0·60	6
0·61 to 0·70	7
0·71 to 0·80	6
0·81 to 0·90	4
0·91 to 1·00	0
1·01 to 1·10	0
1·11 to 1·13	2
Total number of samples examined	43

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THE BRITISH PHARMACOPOEIA ANTIMONY TRICHLORIDE COLOUR TEST FOR COD-LIVER OIL

IT is apparent that there is considerable doubt among chemists as to how to recognise the colour specified in the British Pharmacopoeia, 1932, in the test for cod-liver oil by the antimony trichloride reaction.

The limit recommended in this test corresponds with the colour of the Lovibond blue glass, No. 6·0.

THE COLOUR LABORATORY, MILFORD, SALISBURY

THE TINTOMETER, LTD.

THE DETERMINATION OF META- AND ORTHO-CRESOLS

SINCE the publication of our method for the determination of meta- and ortho-cresols in THE ANALYST (1932, p. 567) we have found that the precipitation of the aldehyde resins is best effected by cooling the liquid to 50° C. before adding the hydrochloric acid, and by subsequent dilution with a further 25 c.c. of water.

This always yields a fine precipitate, free from other compounds which might become occluded if the separated solid is aggregated in lumps, and it may be readily washed clean and dried to constant weight at 100° C. before filtration.

We have received evidence that other workers can obtain concordant results, provided the resin is precipitated in a finely-divided condition, and this is ensured by following the modified procedure outlined above.

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Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

ESSENTIAL OILS. REPORT No. 10

THE DETERMINATION OF CITRONELLAL

THE Essential Oil Sub-Committee recommends the following modification of the hydroxylamine method for the determination of citronellal. This has been found to give excellent results in practice, but certain precautions are necessary as the reaction between citronellal and hydroxylamine hydrochloride takes place rapidly in the cold in a slightly acid solution, but very slowly in alkaline solution. In addition citronellal is rapidly destroyed by free hydrochloric acid, so that it becomes important to neutralise, as quickly as possible, the free acid liberated in the reaction. At the same time the reaction mixture must not be allowed to become alkaline. The following solutions are required:

Indicator Solution.—A 0·2 per cent. solution of dimethyl-yellow (*p*-dimethylaminoazobenzene) in 90 per cent. alcohol.

N/2 Alcoholic Potash.—Prepared with 90 per cent. (by volume) alcohol and standardised against *N*/2 hydrochloric acid, using dimethyl yellow as indicator and running the alkali into the acid until the full yellow colour is obtained.

N/1 Hydroxylamine Hydrochloride Reagent.—Dissolve 6·95 grms. of pure hydroxylamine hydrochloride in 95 c.c. of 90 per cent. (by volume) alcohol, add 0·4 c.c. of dimethyl yellow solution, adjust to the full yellow colour of the indicator with *N*/2 alcoholic potash, and make up to 100 c.c. with 90 per cent. (by volume) alcohol.

The alcohol used must be free from aldehydes and ketones.

The full yellow colour of the indicator may be defined as that colour which is not changed by the further addition of alkali. The correct adjustment of the reagent should be confirmed in the following manner:

Place 10 c.c. in each of two tubes, and to one tube add 1 drop of $N/2$ alcoholic potash; no change in colour should be observed. To the other tube add 1 drop of $N/2$ hydrochloric acid; a slight change in colour towards orange should be produced.

METHOD OF DETERMINATION.—Into a stoppered tube approximately 150 mm. long by 25 mm. diameter, weigh accurately such a quantity of the oil as contains about 0·8 grm. of citronellal and cool to a temperature of 0° (or lower). Add about 10 c.c. of the $N/1$ hydroxylamine hydrochloride reagent previously cooled to 0°, and titrate the liberated acid *immediately* with $N/2$ alcoholic potash, adding the alkali very cautiously and *taking great care to avoid going beyond the orange colour of the indicator.* Continue the titration as long as the red colour develops, then allow the mixture to stand at laboratory temperature for 1 hour and complete the titration to the full yellow colour of the indicator.

The number of c.c. of $N/2$ alcoholic potash required, multiplied by the correcting factor 1·008, by the factor 0·077 for citronellal, and by 100, and divided by the weight of oil taken, will give the percentage (by weight) of the aldehydes, calculated as citronellal.

The correcting factor is necessary owing to the fact that the end-point of the titration occurs at a p_H different from that of normal hydroxylamine hydrochloride.

The results of determinations of citronellal in a sample of Java citronella oil circulated to the members of the Sub-Committee are given in the following table. We are of opinion that the maximum variation in the percentage of citronellal, as determined by this method, should not exceed ±0·5 per cent.

PERCENTAGE OF CITRONELLAL IN JAVA CITRONELLA OIL

Sub-Committee Member	
1.	33·0
	33·3
2.	32·8
	32·9
3.	33·2
4.	33·4
	33·4
	33·2
5.	33·1
	33·4
6.	33·1
	33·1
	33·2
	33·3
7.	33·5
	33·7
	33·8
8.	33·2
	33·8
9.	32·9
	33·1
Variation	32·8 to 33·8
Mean	33·26

(*Signed*),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, W. H. Simmons, T. Tusting Cocking (Hon. Sec.).

21*st September,* 1932

Bibliography on Heavy Metals in Food and Biological Material

(*From the beginning of the year 1921 to date*)

II LEAD

Allport and Skrimshire. New Method for the Determination of Lead in Organic Material, with Special Reference to Dyestuffs. Analyst, 1932, 440. (Colorimetric as sulphide.)

Andrew. Colorimetric Estimation of Lead in Cream of Tartar. Analyst, 1924, **49**, 129. (With potassium cyanide and ammonia.)

Anon. Fairhall (Chromate) Method for Determining Minimal Amounts of Lead in Faecal Specimens. *Ind. Eng. Chem.*, 1926, **18**, 431; *B.C.A.*, 1926, 592A.

Avery, Hemingway, Anderson, and Read. Determination of Minute Amounts of Lead in Water, with Notes on Certain Causes of Error. *Proc. Austral. Inst. Min. Met.*, 1921, 173; *J.S.C.I.*, 1922, 154A.

Avery, Hemingway, Anderson, and Read. Determination of Minute Amounts of Lead. *Chem. Eng. Mining Rev.*, 1921, **14**, No. 157, 30; *C.A.*, 1922, 601. (Colorimetric as sulphide, in waters.)

Bailey. Report on Baking Powder. *J.A.O.A.C.*, 1922, **5**, 514; *C.A.*, 1922, 3137. (Chittick method recommended tentatively for lead.)

Bailey. Report on Baking Powder. *J.A.O.A.C.*, 1923, **6**, 445; *C.A.*, 1923, 2621. (Report on electrolytic determination of lead.)

Bailey. Report on Baking Powder. *J.A.O.A.C.*, 1924, **8**, 91; *C.A.*, 1925, 544. (Electrolytic method recommended for lead.)

Bailey. Report on (Analysis of) Baking Powder. *J.A.O.A.C.*, 1925, **8**, 490; *C.A.*, 1925, 3132. (Electrolytic, for lead.)

Baker. Lead in Soda Water. Report of the Palestine Department of Public Health for the Year 1926. Analyst, 1928, **53**, 97.

Barth. Lead Content of Human Bones. *Arch. path. Anat. Physiol.*, 1931, **281**, 146; *B.C.A.*, 1932, 294A. (Schmidt's micro-method used.)

Behrens and Behrens. Pharmacology of Lead. VI, Method for the Determination of Small Quantities of Lead. *Arch. expt. Path. Pharmacol.*, 1932, **164**, 501; *C.A.*, 1932, 3272. (Method for urine.)

Berg. Occurrence of Unusual Elements in Foods, and in Human Excreta. *Biochem. Z.*, 1925, **165**, 461; *B.C.A.*, 1926, 195A. (Copper, zinc, lead and other metals found in excreta.)

Berg. Determination of Minute Traces of Lead in Biological Material. *Biochem. Z.*, 1928, **198**, 420; *B.C.A.*, 1928, 1292A. (The peroxide is deposited electrolytically.)

Bernhardt. Determination of Very Small Quantities of Lead in Animal Tissues, and the Ageing of Very Dilute Solutions of Lead Nitrate. *Z. anal. Chem.*, 1925, **67**, 97; Analyst, 1925, **50**, 574. (Electrolytic deposition of lead dioxide, followed by iodimetric determination.)

Berry. Report on (Determination of) Lead (in Foods). *J.A.O.A.C.*, 1931, **14**, 452; *C.A.*, 1932, 775. (Gravimetric as chromate.)

Bertrand and Ciurea. Lead in the Animal Organism. *Compt. rend.*, 1931, **192**, 990; *B.C.A.*, 1931, 756A.

Beythien. Metal Tubes for Cosmetics. *Z. Nahr. Genussm.*, 1922, **43**, 47; *C.A.*, 1922, 2571. (Lead and tin found in contents.)

Bishop. Occurrence of Lead in Hen's Eggs. *Med. J. Austral.*, 1928, i, 480; *B.C.A.*, 1929, 340A. (Nessler method in alkaline solution.)

Bishop. Occurrence of Lead in the Egg of the Domestic Hen. *Med. J. Austral.*, 1929, I, 96; *C.A.*, 1929, 3992.

Bishop. Occurrence of Metallic Elements in Biological Material. *J. Cancer Res. Comm. Sydney*, 1930, **1**, 242; *B.C.A.*, 1930, 632A. (Lead found.)

Bishop and Cooksey. Occurrence of Lead in the Egg of the Domestic Hen. *Med. J. Austral.*, 1929, **2**, 660; *B.C.A.*, 1931, 380.

Brüning and Kraft. Fatal Case of Acute Lead Poisoning. *Arch. Pharm.*, 1928, **266**, 501; *B.C.A.*, 1928, 1399A. (Method of examination.)

Büll. Detection of Small Amounts of Lead and Mercury in the Organism. *Biochem. Z.*, 1931, **230**, 299; *B.C.A.*, 1931, 662A. (Lead as potassium-copper-lead nitrite.)

Chapman and Linden. Presence of Lead and other Metallic Impurities in Marine Crustaceans and Shell Fish. Analyst, 1926, **51**, 563.

Christiansen, Hevesy, and Lomholt. Distribution of Lead in the Living Organism. *Compt. rend.*, 1924, **179**, 291; Analyst, 1924, **49**, 490. (The equilibrium between the lead in solution and the β-rays of radium E is used to determine the lead.)

Clarke. Report on (Determination of) Metals in Foods. *J.A.O.A.C.*, 1926, **9**, 364; *C.A.*, 1927, 282. (Colorimetric determination of lead.)

Collin and Sand. The Electrolytic Separation of Lead and Antimony and its Application to the Determination of Lead in Tartar Emetic. Analyst, 1931, **56**, 90.

Cooksey and Walton. Electrolytic Determination of Lead in Urine. Analyst, 1929, **54**, 97.

Danckwortt and Jürgens. Toxicology of Lead and its Compounds. IV, Electrolytic Detection. V. Nephelometric Determination. *Arch. Pharm.*, 1928, **266**, 367, 374; *B.C.A.*, 1928, 981a.

Danckwortt and Jürgens. Toxicology of Lead and its Compounds. VI. Distribution of Lead in the Organism, especially in the Bones, and the Toxicity of Lead Solutions to Fish. *Arch. Farm.*, 1928, **266**, 492; *B.C.A.*, 1928, 1399a. (Method for determining lead in the bones.)

Danckwortt and Ude. Toxicology of Lead and its Compounds. *Arch. Pharm.*, 1926, **264**, 712; *B.C.A.*, 1927, 277a. (The chromate or triple-nitrite test is used; *cf.* Fairhall.)

Dott. The Arsenic and Lead Limits of the B.P. *Pharm. J.*, 1923, **110**, 138; *C.A.*, 1923, 2033.

Dutoit and Zbinden. Spectrographic Analysis of the Ash of Blood and of Organs. *Compt. rend.*, 1929, **188**, 1628; *B.C.A.*, 1929, 952a.

Fairhall. Lead Studies. I. Estimation of Minute Amounts of Lead in Biological Material. *J. Ind. Hyg.*, 1922, **4**, 9; *J.C.S.*, *Abs.*, 1922, ii, 659. (Iodimetric.)

Fairhall. Rapid Method of Testing Urine for Lead. *J. Biol. Chem.*, 1924, **60**, 485; Analyst, 1924, **49**, 490. (Volumetric by chromate method.)

Fischer and Huppmann. Detection of Lead in the Urine. *Süddeutsche Apoth. Ztg.*, 1931, **71**, 603; *B.C.A.*, 1932, 774a. (As potassium-copper-lead nitrite.)

Fischleber. Arsenic and Lead Contents of Fruit Wines. *Wein und Rebe*, 1931, **13**, 107; *C.A.*, 1932, 4678.

Fox. Lead in Self-raising Flour. Analyst, 1922, **47**, 468.

Francis, Harvey, and Buchan. Determination of Small Quantities of Lead, with Special Reference to Urine and Biological Materials. Analyst, 1929, **54**, 725. (Colorimetric as sulphide.)

Fretwurst and Hertz. Determination of Lead in Faeces and Urine and its Significance for the Diagnosis of Lead Poisoning. *Arch. Hyg.*, 1930, **104**, 215; *B.C.A.*, 1931, 518a. (Precipitation as chromate, titration with thiosulphate.)

Friedberger and Hashimoto. Testing for Lead dissolved in Water by the Biological Method of Friedberger. *Z. Hyg. Infektionskrankh.*, 1929, **110**, 755; *C.A.*, 1930, 2484.

Froboese. Determination of Lead in Organic Substances, especially Urine and Faeces. *Arch. Hyg.*, 1926, **96**, 289; *C.A.*, 1927, 2710. (As chromate.)

Ganassini. Determination of Lead in Body-Fluids and Tissues. *Arch. Ist. Biochim. Ital.*, 1929, i, 105; *B.C.A.*, 1929, 955a. (Precipitated as sulphide and identified as iodide; other tests also given.)

Gelman. Clinical Observations in Lead Poisoning. *Arch. Hyg.*, 1926, **96**, 301; *C.A.*, 1928, 3930. (Determination as sulphate.)

Gerlach and Gerlach. Detection of Lead in Organic Tissues. *Naturwissenschaften*, 1931, **19**, 111; *B.C.A.*, 1931, 662a. (Spectroscopic.)

Greenburg. A Source of Lead Contamination of Cistern Water. *U.S. Public Health Reports*, 1922, **37**, 1825; *C.A.*, 1922, 3722. (Contamination from the lead flashing of the roof.)

Griffiths-Jones. Lead and Arsenic in Tartar Emetic. *Lancet*, 1926, **210**, 194; Analyst, 1926, **51**, 201. (Gravimetric.)

Hamence. Separation and Determination of Traces of Lead in the Presence of Small Quantities of Iron. Analyst, 1932, **57**, 622. (Application to organic substances referred to.)

Hansma. Detection and Estimation of Lead in Some Articles of Commerce. *Pharm. Weekblad*, 1922, **59**, 1314; *C.A.*, 1923, 509. (By means of chromate.)

Hartzell and Wilcoxon. Analysis of Sprayed Apples for Lead and Arsenic. *J. Econ. Entomol.*, 1928, **21**, 125; *B.C.A.*, 1928, 622b.

Henderson. Lead in Soda Water. Report of the Queensland Government Analyst for the Year ending June 30, 1927. Analyst, 1928, **53**, 39.

Henderson. Lead in Soda Water Fountains. Report of the Queensland Government Analyst for the Year ending June 30, 1928. Analyst, 1928, **53**, 652.

Henderson. Lead in Soda Water. Report of the Queensland Government Analyst for the Year ending June 30, 1929. Analyst, 1929, **54**, 747.

Henderson. Lead and Arsenic in Cabbages. Report of the Queensland Government Analyst for the Year ending June 30, 1928. Analyst, 1928, **53**, 653.

Henderson. Lead Arsenate in Cabbages. Report of the Queensland Government Analyst for the Year ending June 30, 1929. Analyst, 1929, **54**, 747.

Henderson. Lead Arsenate in Cabbage. Report of the Queensland Government Analyst for the Year ending June 30, 1930. Analyst, 1931, **56**, 32.

Hevesy. Use of Radioactive Indicators in Biology. *Biochem. Z.*, 1926, **173**, 175; *C.A.*, 1927, 752. (For determining lead, etc.)

Howard. Lead in Drinking Water. *Amer. J. Pub. Health*, 1923, **13**, 207; *C.A.*, 1923, 1680. (0·25 p.p.m. may cause poisoning, although an arbitrary limit of 0·5 p.p.m. has been adopted.)

Jackson and Jackson. Devonshire Colic (Lead Poisoning) due to Cider. *Lancet*, 1932, **223**, 717; Analyst, 1932, 792. (Colorimetric as sulphide.)

Järvinen. Colorimetric Estimation of Small Quantities of Metals in Foodstuffs and the Preliminary Destruction of the Organic Matter. *Z. Nahr. Genussm.*, 1923, **45**, 183; *J.C.S., Abs.*, 1923, ii, 655. (Method for lead given.)

Kawata. Do Tumour Cells possess a Specific Affinity for Lead? *Beitr. Path. Anat.*, 1929, **82**, 259; *C.A.*, 1930, 886. (Determination by radio-activity.)

Kielhöfer. Lead Content of Must and Wine from Grapes treated with Insecticides containing Lead. *Z. Unters. Lebensm.*, 1929, **58**, 382; Analyst, 1930, **55**, 151.

Klostermann. Determination of Small Quantities of Lead in Organs by Chemical and Spectrographic Means. *Ver. Ges. deut. Naturforsch. Aerzte*, 1926, **3**, 1116; *B.C.A.*, 1927, 376A. (Colorimetric, with lead dioxide, tetramethyldiaminodiphenylmethane, and glacial acetic acid; also spectrometric.)

Kohn-Abrest. New Data on Saturnism. *Chim. et Ind.*, 1929, 741; *C.A.*, 1929, 4281. (Determination of the lead as chromate.)

Lendrich and Mayer. Occurrence of Arsenic and Lead in Fruit as a Result of Treatment with Protecting Agents. *Z. Unters. Lebensm.*, 1926, **52**, 441; Analyst, 1927, **52**, 237. (Lead determined by Winkler's method.)

Lendrich and Mayer. Occurrence of Arsenic, Lead, and Copper in Fruit and Fruit Products as a Result of Spraying. *Z. Unters. Lebensm.*, 1927, **54**, 137; *B.C.A.*, 1927, 954B.

Liebknecht and Gerb. Colorimetric Determination of Lead, especially in Water. *Z. angew. Chem.*, 1932, **45**, 744. (As sulphide, in presence of a colloid.)

Liversedge. Gravimetric Electro-deposition of Metals and its Application to Pharmaceutical Chemicals, II. *Quart. J. Pharm.*, 1930, **3**, 482; *B.C.A.*, 1931, 68B. (Method for lead.)

Lomholt. Distribution of Lead in the Organism on the Basis of a Photographic (Radiochemical) Method. *J. Pharm. Exp. Ther.*, 1930, **40**, 235; *B.C.A.*, 1931, 119A.

Lynch, McDonnell, Haywood, Quaintance, and Waite. Poisonous Metals on Sprayed Fruits and Vegetables. *U.S. Dep. Agric.*, 1922, *Bull.* 1027, 1; *C.A.*, 1922, 2006. (Lead [and copper] found in only small amounts, if spraying properly executed.)

Macheboeuf, Cheftel, and Blass. Colorimetric Determination of Small Quantities of Lead introduced into Foodstuffs. *Compt. rend.*, 1932, **195**, 146; *C.A.*, 1932, 4886. (Colorimetric as sulphide.)

Mains. Report on Baking Powder. *J.A.O.A.C.*, 1922, **5**, 179; *C.A.*, 1922, 1814. (Electrolytic method for lead.)

McCarthy. Report on [Determination of] Lead [in Foods]. *J.A.O.A.C.*, 1932, **15**, 370; *C.A.*, 1932, 5349. (Colorimetric with *s*-diphenylcarbamide.)

Meyer. New Reaction for Dyestuffs containing Copper in Hair and its Use in the Identification of Dye in Hair. *Chem.-Ztg.*, 1932, **56**, 95; Analyst, 1932, **57**, 333. (Detection of lead mentioned.)

Minot. Electrolytic Estimation of Lead in Biological Work. *J. Biol. Chem.*, 1923, **55**, 1; Analyst, 1923, **48**, 185. (Fairhall's chromate method preferable to Denis and Minot's electrolytic method.)

Nakaseko and Nakano. Determination of Small Amounts of Lead in Animal Tissues. *Kyoto Med. J.*, 1925, **22** (8); *J.C.S., Abs.*, 1925, ii, 1205. (Precipitation as sulphide and chromate consecutively, followed by iodimetric determination.)

Necke, Schmidt, and Klostermann. Determination of Minute Quantities of Lead. *Deut. Med. Wochenschr.*, 1926, **52**, 1855; *C.A.*, 1927, 1284. (Colorimetric, in tissues.)

Neukam. Lead in Tube Preparations. *Chem.-Ztg.*, 1921, **45**, 301; *C.A.*, 1921, 2150. (Dentifrices, face creams, etc., show lead in appreciable amounts.)

Owe. Detection of Tin and Lead in Preserves and Containers. *Z. Unters. Lebensm.*, 1926, **51**, 214; *B.C.A.*, 1926, 606B. (Lead precipitated as chromate and this determined iodimetrically.)

PATTEN. Report on Baking Powder. *J.A.O.A.C.*, 1921, **4**, 538; *C.A.*, 1921, 3880. (Method for lead given.)

PATTEN and MAINS. Determination of Lead in Phosphate Baking Powders. *J.A.O.A.C.*, 1920, **4**, 235; *J.S.C.I.*, *Abs.*, 1921, 159.

PETHERICK. Lead in Carbonated Beverages. *Ann. Rep. of Public Health to June* 30, 1927 (Gt. Britain); *C.A.*, 1928, 2998.

PETHERICK. Investigation of Soda Water for Lead. *Bull. Hyg.*, 1928, **3**, 402; *B.C.A.*, 1929, 418B.

PFYL and SAMTER. Alkalinity of the Ash of Foodstuffs. II. Experimental Groundwork. Simultaneous Titration of a Series of Ash Components. *Z. Nahr. Genussm.*, 1923, **46**. 241; *J.C.S.*, *Abs.*, 1924, ii, 276. (Method for lead given.)

PYRIKI. Colorimetric Estimation of Lead and Copper in Water. *Z. anal. Chem.*, 1924, **64**, 325; ANALYST, 1924, **49**, 491. (With slight adjustment, Winkler's ferrocyanide and sulphide method for determining lead and copper simultaneously is satisfactory.)

RICHARDSON. Determination of Minute Amounts of Lead and Copper in Food, Beverages, etc, ANALYST, 1930, **55**, 323. (Colorimetric with hydrogen sulphide.)

ROFF. Arsenic and Lead Limits of B.P. *Pharm. J.*, 1930, **124**, 506; *C.A.*, 1930, 5433. (Inconsistencies indicated.)

ROSENTHALER. Economical Drug Testing. *Pharm. Ztg.*, 1929, **74**, 1279; *C.A.*, 1930, 462. (Microchemical test for lead.)

SALE. Report on Water. *J.A.O.A.C.*, 1922, **5**, 379; *C.A.*, 1922, 2563. (Lead determined colorimetrically as sulphide.)

SALE. Report on Water. *J.A.O.A.C.*, 1923, **6**, 307; *C.A.*, 1923, 1853. (Method for lead given.)

SCHMIDT. Determination of Minute Amounts of Lead. *Deut. med. Wochenschr.*, 1928, **54**, 520; *B.C.A.*, 1928, 1347A. (Combined electrolytic and colorimetric determination of lead in tissues.)

SCHMIDT. Present Status of Experimental and Clinical Research on the Cause of Lead Poisoning. *Zentr. Gewerbehyg. Unfallverhüt.*, **14**, 180; *C.A.*, 1928, 4641. (Colorimetric determination.)

SCHÜTZ. Detection of Lead and Copper Salts in Citric and Tartaric Acids. *Pharm. Ztg.*, 1929, **74**, 1127; *B.C.A.*, 1930, 36B. (Critical study of officinal [D.A.B.VI] German methods.)

SCHUMM. Detection of Small Quantities of Lead in Urine. *Z. physiol. Chem.*, 1922, **118**, 189; *J.C.S.*, *Abs.*, 1922, ii, 317. (Lead precipitated as sulphide together with copper sulphide and mixture separated electrolytically.)

SCOTT. Determination of Lead in Minute Quantity. *Chem. News*, 1925, **131**, 17; *J.S.C.I.*, 1925, 654B. (Colorimetric as sulphide.)

SEISER, NECKE, and MÜLLER. Electrolytic Determination of Small Quantities of Lead. *Z. angew. Chem.*, 1929, **42**, 96; *B.C.A.*, 1929, 286A. (Lead dioxide, deposited electrolytically, is determined colorimetrically with tetramethyldiaminodiphenylmethane.)

SEISER, NECKE, and MÜLLER. Micro-determinations of Lead (Diagnosis of Lead Poisoning). *Arch. Hyg.*, 1928, **99**, 158; *C.A.*, 1929, 173. (Colorimetric with tetramethyldiaminodiphenylmethane.)

SELF. The Arsenic and Lead Limits of the B.P. *Pharm. J.*, 1922, **109**, 464; *C.A.*, 1923, 1302.

SETTIMJ. Micro-determination of Lead in Urine. *Ann. Chim. anal. Chim. appl.*, 1931, **13**, 129; *B.C.A.*, 1931, 863A.

SHELDON and RAMAGE. Spectrographic Analysis of Human Tissues. *Biochem. J.*, 1931, **25**, 1608; *B.C.A.*, 1931, 1442A. (Lead occurs spasmodically.)

SHIKATA, TACHI, and HOZAKI. Application of the Polarograph to the Analysis of Abnormal Mineral Constituents. *Bull. Agr. Chem. Soc. Japan*, 1927, **3**, 52; *C.A.*, 1928, 930. (Determination of lead.)

SPENCER. Report on (Determination of) Metals in Foods. *J.A.O.A.C.*, 1931, **14**, 434; *C.A.*, 1932, 774. (Methods for lead discussed.)

TANNAHILL. Determination of Lead in Biological Material. *Med. J. Austral.*, 1929, i, 195; *B.C.A.*, 1930, 1486A. (For small quantities, Avery, Hemingway, Anderson and Read's colorimetric method; for larger, Fairhall's titrimetric method.)

TAYLOR. Determination of Lead in Urine. *J. Proc. Roy. Soc. N.S.W.*, 1927, **61**, **315**; *B.C.A.*, 1928, 1152A. (Nephelometric as sulphide.)

TAYLOR. Criticism of Recent Work on the Presence of Lead in the Egg of the Domestic Hen. *Med. J. Austral.*, 1930, **1**, 675; *C.A.*, 1931, 3716. (Errors of Bishop's method indicated.)

THRESH. So-called Action of Water on Lead (Colorimetric Determination). ANALYST, 1921, **46**, 270. (As sulphide.)

THRESH. Estimation of Lead in Potable Waters and in Urine. ANALYST, **1924, 49**, 124. (Colorimetric as sulphide.)

TICKLE. Lead in Peaty Waters. ANALYST, 1921, **46**, 240. (Precipitation by permanganate and detection as lead sulphide.)

TÖDT. Lead Poisoning from Drinking Water. *Zentr. Gesundheitstech.*, 1931, **3**, 8; *C.A.*, 1932, 5680. (Maximum allowed is 0·3 mgrm. per litre in Germany, and 0·025 to 0·1 mgrm. per litre in America.)

TROTMAN and SUTTON. Estimation of the Inorganic Impurities in Gelatin. ANALYST, 1924, **49**, 271. (Method for lead given.)

WEYRAUCH. Absorption of Lead and its Distribution in the Organism in Experimental Poisoning. *Z. Hyg. Infektionskrankh.*, 1930, **111**, 162; *C.A.*, 1930, 3560. (Precipitation as sulphide, electrolysis, and colorimetric determination successively.)

WILLIAMS. Lead in Tinned Corn Beef. ANALYST, 1927, **52**, 28.

WIRTHLE and AMBERGER. Tea containing Lead. *Z. Nahr. Genussm.*, 1922, **44**, 89; ANALYST, 1922, **47**, 478. (Lead introduced mechanically and by corrosion. Infusions with tap water also contained lead.)

WOOD. Detection of Small Quantities of Lead in the Tissues. *J. Cancer Research*, 1930, **14**, 476; *C.A.*, 1930, 5858.

ZBINDEN. The Infinitely Small Quantities of Certain Elements in Milk and their Detection by the Spectrographic Method. *Lait*, 1931, **11**, 114; *C.A.*, 1931, 4032. (Lead found regularly.)

ZELLNER. Lead in Sardines in Oil. *Deut. Nahrungsm. Rundschau*, 1929, **4**, 23; *C.A.*, 1929, 3520. (Fifty per cent. of samples examined contained lead.)

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

ANNUAL REPORT OF THE CITY ANALYST FOR 1931

OF the 6009 samples submitted for analysis, 5003 were taken in connection with the Sale of Food and Drugs Act, and included 2617 milks (238 incorrect), 446 butters (2 incorrect), 258 margarines (1 incorrect), and 106 lards (all genuine). The total percentage returned as incorrect was 6·3.

"EXTRA CREAM ICE."—Twelve samples of ice cream and cream ice contained butter-fat in amounts varying from 2 to 24 per cent. In the absence of any legal standard for ice cream, all the samples but one were passed as genuine. This was described on the label as "Extra Cream Ice," which would lead the purchaser to suppose he was getting an article superior to ordinary cream ice, which itself should contain more fat than ice cream. The sample contained only 2 per cent. of fat, which was the smallest amount found in any of the samples. It was returned as being falsely labelled.

CHALK IN SWEETS.—Samples of sweets, in the form of tablets, contained a core of flavoured chocolate covered with a film of gum, followed by a layer of French chalk and chalk, the whole being covered with coloured sugar. The total extraneous mineral matter was over 10 per cent., and the manufacturers were asked for an explanation. Among other reasons for the inclusion of the chalk, it was claimed that it would help to make good the deficiency in calcium in the ordinary diet, and so would be beneficial rather than harmful. Finally, however, they agreed to manufacture the tablets in such a way as to avoid the use of chalk or other insoluble matter.

"FRUIT DRINKS."—Analysis of three samples of mineral waters, described as "Fruit Drinks," showed that they contained no genuine fruit juice, the ingredients being citric acid, the essential oil of the fruit mentioned on the label, and sugar. The makers agreed to withdraw the term "Fruit Drink."

H. H. BAGNALL

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

TRADE DESCRIPTION OF WINES

ON October 31st a firm of British wine manufacturers was summoned at Clerkenwell Police Court for selling, contrary to the Merchandise Marks Act, 1887, certain bottles of liquor to which a false trade description (*e.g.* sauterne, burgundy, chablis, vermouth) had been applied.

Mr. Monier-Williams, for the prosecution, contended that the contents of the bottles were quite different from the genuine products connoted by the respective names, and that the labels were calculated to lead the purchaser to think that he was getting the genuine wines.

The defence was that the liquors were produced from musts from grapes grown in Sardinia.

The Magistrate (Mr. Pope), in giving judgment, said that these wines were made from imported musts, and he had been asked to say that such names as "burgundy" had become generic terms and were no longer confined to the products of the Continental countries from which they had originated. There might be strong reasons for getting that view promulgated under competent authority, but the governing idea of the Statute was the idea created in the mind of the public.

He held that the use of the words "sauterne," "burgundy," etc., was fundamentally untrue, even with the addition of the letters "P.M.P." (meaning Pure Must Product), which the public would not understand. Why make such free use of French names if there was no intention to mislead? Referring to the "French vermouth," the Magistrate said that, as the word "type" had been added, it would not be fair to convict in that case, but the "Italian vermouth" was presented in such a way as to amount to a false trade description.

He imposed a fine of 40s. in each of the seven cases, with five guineas costs on each summons.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1931

THE Government Analyst (Dr. J. G. Willimott) states that 1749 samples were examined, of which 778 were food and drugs and 449 were in connection with criminal cases. Of the 88 samples of food and drugs found to be adulterated, 58 were of coffee and 14 of milk. Some form of starch was used for the adulteration of the coffee, and the milk was either skimmed or watered. It appears that lye water, prepared from wood ashes, is frequently used as an adulterant of milk, the idea being that the specific gravity is not thereby affected.

LABELLING OF FOOD AS "ADULTERATED."—Many shopkeepers, presumably on legal advice, have adopted the sharp practice of labelling every foodstuff as "adulterated," in the belief that by so doing the vendor renders himself immune from prosecution. From certain decisions given in the Courts it would appear that practices of this nature are legally permissible.

CASES OF ANIMAL POISONING.—Five of twenty viscera taken from the different farm animals of Cyprus were found to contain white arsenic. A certain amount of the arsenic used in the past for the destruction of locusts is still in the hands of the villagers, and is thus easily available when any poisoning is to be done.

QUININE POISONING.—A fatal case of quinine poisoning occurred at Amiandos, where a girl, five years old, swallowed 25 five-grain tablets of sugar-coated quinine tablets in the belief that they were sweets. Vomiting and purging soon came on, followed by cyanosis, collapse, and death within three hours. Quinine was found in the stomach and traces in the liver. Particulars of the *post-mortem* examination were published in the *Lancet* of November 21st, 1931.

PIGMENTS OF THE POLLEN OF CERTAIN LILIES.—The pollen and anthers of certain lilies yield, on suitable extraction, a pigment which can act as a sensitive indicator with acid and alkali. The colour in dilute acids is a pink-red and in dilute alkalis a bright green, the end-point being remarkably sharp. In titration work these indicators were found to give the same results as methyl red or litmus. The best method of extraction is one of simple maceration of the anthers at room temperature. When extraction of the indicator pigment is attempted in 90 per cent. alcohol, several other pigments are extracted at the same time, thus giving a heterogenous solution. The confusing pigments consist of a considerable amount of carotene, a little xanthophyll and another unknown pigment. The indicator pigment is also present in the flowers, from which it was isolated and proved to be an anthocyanin.

Fiji

REPORT OF THE GOVERNMENT CHEMIST FOR THE YEAR 1931

IN his annual report to the Department of Agriculture, Fiji, Mr. J. W. Blackie states that 717 samples were analysed as against 541 in 1930. These included 130 of milk, 51 of other foods, 27 of drugs, and 17 of aerated waters.

MILK.—As a result of the rigid inspection of dairies the milk has been much cleaner than in former years. It has been argued in the past that it is impossible to produce milk in Fiji up to the standard required by law in England, namely, 3·0 per cent. of fat, 8·5 per cent. of solids-not-fat. This feeling has resulted from the consistently poor quality of the milk offered for sale. The figures obtained during this year, which has not been exceptional, show definitely that milk can be produced in Suva of a quality equal to that in temperate countries, and, provided that the herds are healthy, there is no reason why a standard of 3·2 per cent. of fat and 8·5 per cent. of solids-not-fat should not be enforced, instead of the low requirement of the dairy by-laws now in force, namely, 3·0 per cent. of fat and 8 per cent. of solids-not-fat.

The research work carried out during the year included the following investigations:

DIDI RESIN.—The resinous substance exuding from *Canarium vitiensi* is used locally as an adulterant of kauri resin. It was found to contain 26·5 per cent. of a resene (m.pt. 183° to 185° C.), soluble in ether and in chloroform; 53 per cent.

of other resenes, soluble in alcohol; and 5·8 per cent. of an essential oil. The alcohol-soluble portion would have some value as a lacquer for metals.

TOXIC PRINCIPLE OF LANTANA CROCEA.—A strange cattle disease, attributed to ingestion of *Lantana crocea*, was investigated. The veterinary evidence indicated that substances akin to lupino-toxins were present, but, up to the present, these have not been detected. A trace of an alkaloidal substance was isolated, and is under investigation. Feeding experiments and injections with extracts of the plants under examination failed to produce the characteristic lantana symptoms, but, as the veterinary officers obtained positive results with other specimens, it is suggested that there may be seasonal variation in the active principle.

ETHYL ESTERS OF CALOPHYLLUM (DILO) OIL.—The "ethyl esters" of dilo oil, obtained from the kernels of *Calophyllum inophyllum*, were found to consist of about 50 per cent. of unesterified material containing the glycerides of oleic, palmitic and stearic acids, together with resin acids and resenes. The esterified portion contained about 20·6 per cent. of ethyl oleate and 79·4 per cent. of ethyl palmitate and ethyl stearate in approximately equal proportions. The natives use the oil for massaging purposes, and some success has attended the use of the ethyl esters for the treatment of leprosy.

ROTENONE-CONTENT OF DERRIS ULIGINOSA.—The local species of *Derris*, termed *duva* by the natives, has some reputation as a stupefying agent for fish, but, in general, the imported species, *Derris elliptica*, is used. Comparative analyses of the two species showed that the "derrid" content (*i.e.* ethereal extract) of the latter is at least six times as much (*e.g.* 12·0 and 1·8 per cent.). For the determination of the rotenone content the apparatus previously described (*J. Soc. Chem. Ind.*, 1932, **51**, 129T) was used for extracting the material. The following results were obtained with a composite sample of stem and root:—Moisture, 12·2; rotenone on air-dried substance, 0·3; on dry substance, 0·34 per cent. Derris root has been reported to contain as little as a few tenths of a per cent. of rotenone, but the best commercial samples contain from 4 to 5 per cent.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Rapid Method for the Determination of Moisture in Flour and other Finely-divided Materials. E. A. Fisher and J. Thomlinson. (*J. Soc. Chem. Ind.*, 1932, **51**, 355–358T.)—In a patented apparatus (B.P. 365,247), a known weight of the flour is mixed with finely-powdered calcium carbide, the loss in weight of the charged apparatus representing acetylene, from which the moisture reacting with the carbide may be calculated. The method requires calibrating by means of determinations made by the ordinary drying-oven method, as it gives low results, owing to the fact that part of the moisture does not react with the carbide and for other reasons. For the percentage of moisture in a single sample of flour, sixteen pairs of determinations gave results varying from 14·34 to 14·74 by the drying method, and from 13·02 to 13·28 by the method described. The differences between the results obtained simultaneously by the two methods ranged from 1·18 to 1·65, and had the average value 1·36. When the results given by the new method were increased by this average correction, the drying method yielded figures varying from 0·20 below to 0·29 above those of the carbide method. For about 30 commercial flours the two methods gave results differing by 1·20 to 1·90, the average difference being 1·48.

If the loss in weight of the apparatus is determined after the reaction has proceeded for 20 minutes—by which time the system has become reasonably cool—further reaction is comparatively slight with flours containing over 10 per cent. of moisture, but proceeds to an appreciable extent and during a protracted period with flours containing less than 8 or 9 per cent. T. H. P.

Sulphur Content of Foods. K. S. Kemmerer and P. W. Boutwell. (*Ind. Eng. Chem., Anal. Edit.*, 1932, 4, 423–425.)—A quantity of the sample sufficient to contain from 3 to 5 mgrms. of sulphur is digested with nitric acid, and the excess of the acid is evaporated; 10 c.c. of 70 per cent. perchloric acid are then added, and the mixture is boiled until the volume is reduced to about 1 c.c. The excess of perchloric and nitric acids is removed by evaporation with the addition of hydrochloric acid, the residual solution is neutralised with ammonia, boiled, rendered slightly acid with hydrochloric acid, and filtered, and the filtrate is treated with ammonia, then just acidified with hydrochloric acid, litmus being used as indicator, and diluted to a definite volume. The sulphuric acid is then determined, as barium sulphate, in a turbidimeter. A modified Burgess–Parr turbidimeter for the purpose is described. Results of the determination of sulphur in a large number of foods are given, and the following are selected as typical examples:—Apple, 0·018; asparagus, 0·065; red beet, 0·017; white bread, 0·011; whole-meal bread, 0·104; carrots, 0·016; celery, 0·025; cocoa, 0·236; coffee beans, 0·131; garlic, 0·506; lettuce, 0·016; ham, 0·130; beefsteak, 0·202; whole milk, 0·028; mustard seed, 1·175; oatmeal, 0·233; potatoes, 0·049; pepper, 0·035; spinach, 0·030; tea, 0·217; wheat flour (40 per cent. gluten), 0·470 per cent. All the percentages are calculated on the wet substance or on the material as offered for sale. W. P. S.

Precipitation of Sugars and Polyhydric Alcohols by Metallic Hydroxides in Alkaline Media. I. General Character of the Precipitation. P. Fleury and J. Courtois. (*J. Pharm. Chim.*, 1932, 16, 97–109.)—Precipitation of sugars and polyhydric alcohols (glycol, erythritol, mannitol, etc.) from solutions containing a heavy metal salt on addition of an alkali hydroxide appears to be a general reaction. The precipitation is more nearly complete (1) with barium hydroxide than with either ammonium or sodium hydroxide, (2) with iron than with any other of the heavy metals tried, and (3) with acetates of the heavy metals than with nitrates. T. H. P.

Additional Tests in Honey Analysis. J. Grüss. (*Z. Unters. Lebensm.*, 1932, 64, 376–383.)—It is considered that the best honeys should show all the enzymic reactions of the living plant-cell. (1) As a test for oxidase action, 1 grm. of honey is mixed with 5 c.c. of a freshly-prepared solution containing 0·5 to 1 mgrm. of violamine, 5 c.c. of the reagent without honey being placed in a similar vessel as a control. After 2 hours an upper violet and a lower colourless zone should appear in the vessels containing the sample, whilst the control is deep violet throughout. The zones given by different types of honey differ to a pronounced extent in the depth of the coloured zone. For a quantitative determination the mixture is transferred to a flask, and the colourless liquid is titrated with sodium bisulphite solution, or preferably, with a 0·1 *N* solution of sodium thiosulphate in the presence of acetic acid; the values obtained with fruit-, lime-, heather- and robinia-honey were 0·4, 1·0, 1·2, and 1·8 c.c., respectively. The higher the oxidase value the better the honey. (2) The hydrogenase activity is measured by the action of a 10 per cent. solution of honey on an equal weight of milk of sulphur, and the hydrogen sulphide evolved after 2 days at 25 to 28° C. is assessed from the intensity of the stain on a lead acetate paper, or it may be determined exactly by leading it into a solution of a cadmium salt, and weighing the resulting sulphide. (3) One of the usual iodine-starch reactions is used for the evaluation of diastase. The four above-mentioned samples of honey were shown to contain (per grm.) 9005, 1560, 5473, and 1891 grains of pollen, 30, 120, 95, and 335 mould colonies, numerous cocci, and a number of yeast cells. A new yeast (*Anthomyces ruber, n. sp.*) was observed in lime honey and a new *Mucor* mould (*Cephalosporium candidum, n. sp.*) in heather honey. The moulds (which included *Dematia, Penicillia* and *Mucor* types) were usually responsible for the reducing action towards sulphur. J. G.

Specific Test for Orange Honey. R. E. Lothrop. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 395–396.)—Californian orange honey owes its characteristic flavour and aroma to the presence of methyl anthranilate. This substance is not present in honey obtained by bees from other sources. To detect methyl anthranilate 1 kilo. of the honey is dissolved in 800 c.c. of water and steam-distilled; 700 c.c. of distillate are collected and extracted with chloroform, the extract is evaporated in a current of air until the chloroform is just removed, and the residue is dissolved in 2 c.c. of 10 per cent. sulphuric acid. The solution is treated with one drop of 5 per cent. sodium nitrite solution, a few crystals of urea are added to remove excess of nitrous acid, and the solution is added to a mixture of 1 c.c. of 0·5 per cent. β-naphthol solution (in dilute sodium hydroxide solution), 1 c.c. of 10 per cent. sodium hydroxide solution, and 1 c.c. of 10 per cent. sodium carbonate solution. A yellowish-red precipitate is produced if as little as 0·1 mgrm. of methyl anthranilate is present. W. P. S.

Detection and Determination of a Proprietary Oil (Sonderöl) [added to Edible Fats]. H. Schmalfuss and H. Werner. (*Z. Unters. Lebensm.*, 1932, **64**, 362–367.)—The oil, which, according to Schou (E.P. 187,298, 16.11.22), is added to edible fats, is brown in colour, viscous, sparingly soluble in ethyl and propyl alcohols and in petroleum spirit, and readily soluble in all other common organic solvents. Analysis gave: n_D^{40}, 1·467; saponification value, 205; Reichert–Meissl value, 7·5; Polenske value, 8·7; iodine value (Hanus), 51; hydroxyl value, 24·0; acetyl value (Elsbach), 23·0; acid value, 3·0. As a qualitative test 15 c.c. of petroleum spirit (b.pt. 30° to 50° C.) are shaken with 1 grm. of sample in a stoppered tube, when 1 per cent. or more of the oil produces a white opalescence coagulating to a yellow or brown deposit; neither hardened nor blown whale oil react. For quantitative work the insoluble matter from 2 to 30 grms. of sample is removed by filtration, then washed 4 times with petroleum spirit and dried in nitrogen at a low temperature, and weighed. A curve shows the correction for the solubility of the precipitate in the mixture of fat and petroleum spirit. The precipitate contains no sulphur, nitrogen or mineral matter, and all except 0·2 per cent. is saponifiable, the acid precipitated from the resulting soap being partly soluble in petroleum spirit, and partly volatile, and having a mean molecular weight of 256.

J. G.

Composition of Kapok Seed Oil. R. C. Malhotra. (*J. Indian Chem. Soc.*, 1932, **9**, 413.)—Analyses of the oils of *Eriodendron anfractuosum* seeds from Java, Sumatra, and Malaya show wide variations in the composition, which appears to be modified by the time of collection of seeds, methods of storage, age and variety of the parent plant and nature of the soil, as well as by the geographical position.

	Java	Sumatra	Malaya
Sp.gr. at 25° C.	0·9105	0·9216	0·9387
Saponification value ..	170·8	179·2	198·1
Iodine value (Hanus) ..	96·3	95·7	91·3
Saturated acids, per cent...	18·90	17·35	19·60
Unsaturated acids, per cent.	75·98	76·56	75·00

D. G. H.

Castor Oil 135 Years Old. N. Evers. (*Pharm. J.*, 1932, **129**, 372.)—The sample of castor oil 135 years old filled a 4-oz. white glass well-stoppered bottle, and was clear, except for a slight white deposit. The taste, at first bland, became hot and burning to the throat. The colour reading in a 1-in. Lovibond tintometer cell was 2·5 yellow and 0·7 red, and the oil had the following characteristics: Sp.gr. at 15·5°/15·5°C., 0·9652; $n_{\mathrm{D}}^{40^\circ}$, 1·4714; optical rotation, + 6·72°; saponification value, 180; iodine value, 82·6; acetyl value, 148·1; acid value, 15·8; and unsaponifiable matter, 0·6 per cent. The oil was soluble in 3·5 parts of alcohol (90 per cent.), and did not solidify or become cloudy at 0° C. The optical rotation was abnormally high, in fact, equal to that of ricinoleic acid itself, and the acidity was high, but, when fresh, the oil would probably have satisfied present-day requirements.

D. G. H.

Detection of False "Sponge" Essence of Lemon prepared with Machine-extracted Essence. G. Romeo, N. Galletti and J. Amoroso. (*Giorn. Chim. Ind. Appl.*, 1932, **10**, 397–400.)—Essence of lemon extracted mechanically from the peel is utilised almost exclusively for the preparation of concentrated essence by vacuum distillation. The terpenes and the stearoptene obtained in this operation as secondary products are used for making false "sponge" essence. One such procedure consists in adding to the terpenes a certain quantity (2 to 2·5 per cent.) of the stearoptene recovered as residue of the distillation, citral (2 to 2·5 per cent.), sometimes also esters (0·5 to 1 per cent. of linalyl or geranyl acetate), and sufficient of the mechanically-extracted essence to give to the mixture the straw-yellow or greenish-yellow colour characteristic of "sponge" essence. The ordinary physical constants are insufficient to permit such a product to be distinguished from the genuine material, but this can be done by means of the following procedure: Five c.c. of the essence are evaporated on a water-bath until the odour is no longer detectable, the residue being weighed. This residue is treated with a volume of lemon terpenes (obtained by distilling essence of lemon under reduced pressure and collecting the first 20 or 30 per cent. of distillate) representing in c.c. ten times the weight of the residue in grms. After being mixed with a rod at the ordinary temperature, the mechanical essence gives a clear, and true sponge essence, even after filtration, a turbid solution. Moreover, the difference in refractive index between the lemon terpenes used and the solution containing the stearoptene is from 0·0024 to 0·0035 for the mechanical essence, and from 0·0049 to 0·0060 for sponge essence; expressed as readings on the Wollny (Zeiss) butyro refractometer, these figures are 3·9 to 5·8 in the former, and 8·2 to 10 in the latter case. The same procedure allows of the detection in the false sponge essence of the presence of oils, fats or other substances used either in place of, or together with, the stearoptene. T. H. P.

New Arachis Coffee Substitute. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1932, **64**, 389–392.)—Analyses as follows are given for the coffee substitute ("Assamba") and for raw and roasted Chinese arachis nuts, respectively:—Moisture, 4·0, 4·7, 1·0; protein, 23·4, 25·0, 28·0; caffeine, 0·4, 0, 0; mineral matter, 2·42, 1·70, 2·00 (insoluble in hydrochloric acid, 0·04, 0 and 0); reducing sugars, 0·4, 0, 0; extract, 17·8, 12·8, 9·0; fat, 34·8, 47·8, 44·5 per cent. (n^{40}_{D}, 57·5, 55·8, 56·9; acidity, 4·9, 7·6, 2·6); acidity, 8·0, —, 5·6 c.c. *N* NaOH. From these results and from microscopical examination it is calculated that the coffee substitute consists of 33 per cent. of roasted coffee with 5 per cent. of sugar and 62 per cent. of roasted arachis nuts. J. G.

Caffeine in Cereal Beverages. C. H. La Wall and J. W. E. Harrisson. (*Amer. J. Pharm.*, 1932, **104**, 537–539.)—Caffeine, or an infusion or extract of caffeine, or a caffeine-containing ingredient, is sometimes added to cereal beverages. Five brands out of 20 examined in U.S.A., in 1931, contained caffeine in amounts approximating to half a grain to a bottle of the beverage. To detect the caffeine, 100 c.c. of the sample are made slightly alkaline with ammonia and extracted with 25, 15, and successive portions of 10 c.c. of chloroform. The combined extracts are evaporated to dryness, and, if the residue is crystalline, the identification test is applied directly; if not, the residue is purified by the potassium permanganate method of the A.O.A.C. for caffeine in roasted coffee. The identification test consists in adding 15 to 30 mgrms. of potassium chlorate to the dry residue, followed by 1 c.c. of hydrochloric acid. After being mixed the liquid is evaporated to dryness, and a few drops of 10 per cent. ammonium hydroxide solution are allowed to flow over the residue, when the "murexide" purple colour appears in the presence of caffeine. The method may readily be made quantitative.
D. G. H.

Biochemical

Colorimetric Method for the Direct Determination of Urea in Urine. J. F. Barrett and E. B. Jones. (*Biochem. J.*, 1932, **26**, 1246–1250.)—A method for the routine determination of urea in urine is based on the formation of dixanthylurea, a principle described by Fosse (*Compt. rend.*, 1914, **158**, 1076). Interfering substances are removed from the urine with "colloidal iron" (ferric chloride and sodium bicarbonate), and the urea is precipitated from the filtrate by xanthydrol. The precipitate is centrifuged in the presence of barium sulphate, and its nitrogen content is determined colorimetrically after a micro-Kjeldahl digestion. *Reagents required.*—(1) Crystalline ferric chloride in water, 1 per cent. (2) Sodium bicarbonate in water, 0·5 per cent. (3) Barium reagent. Sodium chloride (10 grms.) and sodium sulphate (2 grms.), dissolved in 90 c.c. of distilled water are added to 400 c.c. of glacial acetic acid; 1·2 grm. of barium chloride, dissolved in 10 c.c. of water is added to the mixture. (4) A 2·5 per cent. solution of xanthydrol in glacial acetic acid, kept tightly stoppered, and prepared afresh every few days. (5) Digestion mixture: 100 c.c. of 60 per cent. perchloric acid; 40 c.c. of phosphoric acid (sp.gr. 1·75); 20 c.c. of 3 per cent. sodium selenate solution; 0·5 c.c. of 10 per cent. sodium sulphate solution; 130 c.c. of water. (6) Nessler reagent of Folin and Wu (*J. Biol. Chem.*, 1919, **38**, 81). (7) Ammonium sulphate solution. Pure ammonium sulphate (0·1179 grm.) is dissolved in water, preserved by addition of 2 drops of concentrated sulphuric acid, and diluted to 1 litre. *Procedure.*—To 1 c.c. (or 2 c.c. if the urea-content is low) of urine in a 100-c.c. flask, 2 c.c. of 1 per cent. ferric chloride are added. While the liquid is rotated 10 c.c. of 0·5 per cent. sodium bicarbonate are added, and the whole is diluted to the mark, mixed, and filtered. A suitable amount of filtrate (1 to 5 c.c. depending upon the urea-content) is transferred with an Ostwald pipette to a 4 in. × 1 in. hard glass round-bottomed centrifuge-tube of 35 to 40 c.c. capacity, diluted to 5 c.c. with water, and 5 c.c. of well-mixed barium reagent and 1 c.c. of xanthydrol solution are added. The liquid is mixed and left in a bath of ice-cold water for 20 minutes, mixed again, and the sides of the tube are washed down with 1 c.c. of acetone, which is left on the surface. The tube is centrifuged for five minutes, and the supernatant liquid is decanted, the inverted tube being placed on a sheet of filter-paper for 2 minutes to drain. The excess liquid is removed from the tube by wiping with filter-paper. One c.c. of digestion mixture and a piece of porous earthenware are added, and the tube is gently heated on a sand-bath in a fume cupboard, the mouth of the tube being covered with a watch-glass when heavy white fumes appear and the liquid darkens. Twenty seconds after the brown liquid becomes colourless the tube is removed from the bath, and a few minutes later 20 c.c. of water are added. When the liquid has cooled to room temperature 7·5 c.c. of Nessler reagent are added while the liquid is rotated, and the whole is mixed, and centrifuged for three minutes to remove the precipitate of barium sulphate. The clear supernatant liquid is compared with the standard prepared as follows: Five c.c. of barium reagent and 5 c.c. of water, etc., are placed in a 4 in. × 1 in. tube, centrifuged, drained, and digested as described for the unknown sample. After the liquid has been heated, 15 c.c. of water and 5 c.c. of standard ammonium sulphate solution are added before the addition of 7·5 c.c. of Nessler reagent. The use of a thick blue glass light filter for the comparison in the colorimeter is recommended. *Calculation* (if the standard is set at 20 mm.):

$$\frac{53{\cdot}6}{\text{Colorimetric reading} \times \text{number of c.c. of filtrate used.}} = \text{grms. of urea per 100 c.c. of urine.}$$

Results show close agreement between the xanthydrol and urease methods.

P. H. P.

Determination of Small Quantities of Oxalic Acid [in Urine]. E. C. Dodds and E. J. Gallimore. (*Biochem. J.*, 1932, **26**, 1242–1245.)—A method is described whereby oxalic acid (in urine) can be quantitatively determined. By a preliminary esterification and distillation *in vacuo* from an acid alcoholic solution the oxalic acid is freed from interfering substances, and can then be precipitated as calcium oxalate and the oxalic acid in the precipitate determined gasometrically. The reagents required are: Alcohol, containing dry hydrochloric acid, *N* solution; lime-water, saturated solution, free from carbonate; ammonium phosphate solution, 0·5 per cent. In a 175-c.c. Claisen flask 25 c.c. of urine+1 c.c. *N* hydrochloric acid are evaporated almost to dryness *in vacuo* below 50° C., and the flask is then connected with a receiver (a smaller Claisen flask), which contains 13 c.c. of 4 *N* sodium hydroxide solution, and is kept cool by means of a rapid stream of cold water. To the residue in the flask a mixture of 5 c.c. of alcohol and 2 c.c. of benzene is added, the temperature of the water-bath surrounding the distillation flask is raised to 65° C., and the contents of the flask are dried by distilling off *in vacuo* the low-boiling ternary mixture of alcohol, benzene and water. To remove the last traces of water, it is again distilled with 5 c.c. of acid alcohol and 2 c.c. of benzene. The contents of the flask are boiled with 20 c.c. of the alcohol containing acid on a boiling water-bath for half-an-hour; the flask is then reconnected with the receiver, and the contents are distilled *in vacuo* at 65° C. The vacuum reached about the middle of the distillation should be not less than 30 mm. In all, the boiling and distillation are repeated three times. The slightly alkaline solution in the smaller Claisen flask is evaporated to 10 to 20 c.c. *in vacuo*. To free the oxalic acid from the high concentration of sodium chloride an excess of 2 c.c. 5 *N* hydrochloric acid is added, and the solution is extracted with ether in a continuous extractor for six hours. To the ethereal solution 5 c.c. of water are added, and the ether is removed by distillation. The solution is filtered, if necessary, made alkaline to methyl red with *N*/10 sodium hydroxide, and concentrated to about 3 c.c. on a water-bath. The solution of oxalic acid in 3 to 5 c.c. of water in a centrifuge tube is faintly acidified with *N*/10 acetic acid and mixed with 2 c.c. of saturated lime-water. After the mixture has stood for 12 hours at 0° C., 0·5 c.c. of the ammonium phosphate solution is added. The precipitate is centrifuged, decanted, and washed once with 2 c.c. of water. The oxalic acid in the precipitate is then determined by the gasometric method of Van Slyke and Sendroy (*J. Biol. Chem.*, 1929, **84**, 217). The results obtained with urines by the new distillation method are shown to be appreciably higher than those obtained by ether-extraction of the urines. The principle of the method has also been applied to the determination of oxalic acid in blood, from which small quantities of added oxalic acid have been satisfactorily recovered. P. H. P.

Ultra-Violet Absorption of Certain Vegetable or Animal Oils. A. Chevallier, J. Guillot and P. Chabre. (*Compt. rend.*, 1932, **195**, 678–679.)—The ultra-violet spectra obtained through 1 cm. of 1 per cent. solutions in pure hexane of a number of vegetable and fish oils have been examined between λ 2000 and 4000 Å, and the extinction-coefficients plotted as a curve of the form, $\log I_0/I_x = f(\lambda)$. It was found that pure oils of the same type give curves having the same general characteristics, so that it is possible to distinguish, *e.g.*, pure olive oil from pure maize oil. Individual differences in the chemical nature of oils of the same type correspond with characteristic minor variations in the curves as follows:—*Vitamin A* (*e.g.* in cod-liver oils) produces absorption at 3280 Å (*cf.* the work of Morton and Heilbron). *Unsaponifiable matter* absorbs in a zone between 2550 and 2950 Å, corresponding with the presence of sterol and vitamin *D*. *Free fatty acids* are responsible for absorption bands at 3175 Å, between 2825 and 2625 Å (*i.e.* superimposed on a portion of the band due to unsaponifiable matter), and, in particular, bands covering the region from 2550 Å towards the smaller wave-lengths. *Colouring matters* (*e.g.* chlorophyll) are characterised by bands between 4200 and 3300 Å. J. G.

Reaction of Fish-Liver Oils with Antimony Trichloride. F. Ender. (*Biochem. J.*, 1932, **26**, 1118–1123.)—A certain parallelism exists between the biological activity and the intensity of the blue colour given by liver-oil concentrates of halibut (*Hippoglossus hippoglossus*) with antimony trichloride. At room temperature the blue colour thus formed is exceedingly evanescent, but at −40° C. the reaction-product is stable for hours; at −50° C. a heavy blue oil is precipitated on the bottom of the vessel. The author decided to decompose the blue oil at a low temperature according to the following hypothetical equations:

1. Chromogenic substance (vitamin *A*?) + $SbCl_3$ = blue product.
2. Blue product + H_2O = Chromogenic fraction + $SbOCl$ + $2HCl$.

From the results obtained it is concluded that concentrates of halibut-liver oil probably contain two chromogens, of which one is possibly identical with vitamin *A*, and is destroyed by treatment with antimony trichloride and water, whilst the other, which presumably has no connection with growth in animals, still reacts with antimony trichloride, forming a blue product from which the chromogen may be regenerated by the addition of water. The "chromogenic fraction" formed by the addition of water (pieces of ice or an ice-cold mixture of water and 10 per cent. potassium hydroxide for the neutralisation of the possibly harmful hydrochloric acid) to the blue oil was a reddish-yellow oil; with antimony trichloride it gave about one-third of the colour value given by the original concentrate. The results of the biological experiments seem to justify the conclusion that the antimony trichloride reaction is not specific for vitamin *A*; this is in agreement with the findings of Euler and Euler (*Klin. Woch.*, **1930**, **916**). The absorption bands of the liver-oil concentrate and the "chromogenic fraction," together with the spectra of their reaction products with antimony trichloride, are described. Heilbron, Gillam and Morton (*Biochem. J.*, 1931, **25**, 1352; ANALYST, 1931, **56**, 823) state that the concentrate of halibut-liver oil probably contains two chromogens, of which one causes the absorption at 328*mμ* and that at 583*mμ* of the blue product, and the second causes the absorption at 620*mμ* of the blue product. The author finds that highly active concentrates exhibit with antimony trichloride a decided absorption maximum at 622*mμ*, whereas the inactive preparation (chromogenic fraction) does not, but shows a strong absorption in the neighbourhood of 590*mμ*, and a fainter one at 551*mμ*. On destruction of vitamin *A* subsequent to treatment with antimony trichloride and water, the 622*mμ* band disappears, but the absorption at 590*mμ* is still pronounced. It is, therefore, concluded that an absorption band at 590*mμ* produced by the interaction of antimony trichloride and the "chromogenic fraction" cannot be attributed to vitamin *A*; it is possible, however, that the chromogenic nature of the concentrates after the treatment with antimony trichloride and water may be due to the decomposed vitamin.

P. H. P.

Absorption Spectra of Substances Derived from Vitamin *A*. J. R. Edisbury, A. E. Gillam, I. M. Heilbron, and R. A. Morton. (*Biochem. J.*, 1932, **26**, 1164–1173.)—The blue colour formed in the antimony trichloride colour-test for vitamin *A* is transient. It is possible that the primary process, resulting in the blue colour, leaves the vitamin *A* molecule intact, whilst the secondary reactions associated with the fading of the colour bring about decomposition. The recovery of vitamin *A* from the blue solution by pouring the mixture into much water has been attempted. Partial decomposition of the vitamin occurs, accompanied always by the appearance of narrow absorption bands with maxima at 399, 376, 357 and 340*mμ* (chloroform), and sometimes by additional, less definite maxima, *e.g.* at 425, 324, 308 and 280*mμ*. The wave-lengths at the maxima are constant, irrespective of whether either rich or poor oils or concentrates are used, but the intensities vary roughly with the potency of the material. The oil (or concentrate) obtained is similar in appearance to the original material, and in all cases gives a blue colour with antimony trichloride, similar to, but weaker than, that given by the original. It is claimed that, although the 328*mμ* band cannot be observed as such in the "regenerated" material, its presence, masked by the highly selective absorption of the new products, can be inferred with certainty from the general shape of the absorption curve in conjunction with the results obtained with the colour-test applied to the recovered materials. Recovery of vitamin *A*, although never quantitative, supports the view that the initial reaction is the formation of a vitamin *A* and antimony trichloride loose addition product, but secondary (condensation?) processes probably account for the narrow bands. This view is supported by the observation that the similar maxima 392, 369, 350, 333*mμ* (alcohol) can be obtained with greatly enhanced definition by the action of alcoholic hydrogen chloride on rich concentrates, the intensity, persistence, rate of development and permanence depending on the concentration of hydrogen chloride. Even under optimum conditions the reaction is incomplete, and the product unstable in acids. Neutralisation of the acid with sodium ethoxide arrests the decomposition of the material, but does not effect reversal to vitamin *A*. Similar narrow bands, together with a broad continuous band with its maximum at 290$m\mu$, are shown in certain fractions obtained in slow high vacuum distillation of rich concentrates heated to about 180° C. By prolonged heating at 120 to 125° C. in an atmosphere of nitrogen the development of narrow bands could not be induced to more than a minute extent, but the vitamin nevertheless decomposed fairly readily, the main product exhibiting a maximum at 290$m\mu$. In alcohol at the boiling-point, vitamin *A* is unexpectedly stable to prolonged exposure to a stream of oxygen. After some hours, the 328$m\mu$ maximum decreases in intensity, the absorption in the region 260 to 300$m\mu$ slowly increases, and the narrow absorption bands in the near ultra-violet appear, but with comparatively brief persistence. Ozonised oxygen rapidly destroys vitamin *A* with disappearance of selective absorption, but compounds with maxima at 290$m\mu$ and 272$m\mu$ can be detected in the very early stages. The data are consistent with the vitamin *A* molecule containing a side chain with at least four double bonds, which can be attacked in turn by ozone to give products with broad bands. The hypothesis of ring closure to give hydronaphthalene derivatives as an explanation of the narrow bands will be discussed in a later communication. P. H. P.

Isomerisation of Carotene by Means of Antimony Trichloride. A. E. Gillam, I. M. Heilbron, R. A. Morton, and J. C. Drummond. (*Biochem. J.*, 1932, **26**, 1174–1177.)—The stable blue solution (λ maximum 583 to 590$m\mu$), obtained by the action of antimony trichloride on carotene in chloroform, was poured into water and the organic matter recovered free from antimony. Antimony oxychloride was precipitated and the original colour of the carotene returned. The oxychloride was dissolved in the minimum quantity of concentrated hydrochloric acid, and the mixture was left to stand, when the chloroform layer gradually separated. Red crystals were isolated from the chloroform layer; the melting-point of the purest specimen of crystals obtained was 185° C. The absorption spectrum of the recovered product has been determined in chloroform and carbon disulphide. In both the visible and ultra-violet regions it is quite different from that of carotene. The properties of the substance agree with those of *iso*carotene. P. H. P.

Toxicological and Forensic

Distribution of Chloral Hydrate in the Organism. N. E. Renescu and B. B. Olzsewski. (*Compt. rend.*, 1932, **195**, 624–626.)—Chloral hydrate in 10 per cent. solution was administered, by way of the internal saphenous vein, to dogs (0·25 to 1 grm. per kilo.), and, after death, was found in relatively large quantities in all the organs, and particularly in the brain, liver, kidney, heart and intestines. Chloroform was present in some cases, but only in traces, so that no strong support was obtained for the theory that the narcotic action of chloral hydrate is due to chloroform produced by decomposition. The chloral hydrate content of the blood is relatively high after injection and then decreases rapidly; that of the liver and adipose tissue increases with the duration of narcosis, whilst that of the brain does not appear to be related either to this factor or to the magnitude of the dose. After 2 to 3 months of putrefaction no chloral hydrate remains in the organs. *Chloroform* was determined by distilling 20 grms. of the disintegrated sample with 100 c.c. of 95 per cent. alcohol and 10 c.c. of 20 per cent. tartaric acid into a little 95 per cent. alcohol. The distillate (50 c.c.) was allowed to stand in a stoppered flask for 24 hours with 10 c.c. of a 10 per cent. solution of potassium hydroxide in alcohol, and hydrolysis was then completed by heating for 30 minutes on the water-bath. The chlorides in a solution, in 5 c.c. of dilute nitric acid, of the residue after evaporation, were then titrated with 0·05 *N* silver nitrate solution (1 c.c.$\equiv$1·99 mgrm. $CHCl_3$). *Chloral hydrate* was determined by distillation of the sample with 140 c.c. of water and 20 c.c. of the solution of tartaric acid. When a few drops of distillate no longer gave the resorcinol reaction, a portion (40 c.c.) was saponified by the action of 20 c.c. of the alkali in the presence of 60 c.c. of 95 per cent. alcohol for 24 hours in the cold, followed by 3 hours on the water-bath; after titration in nitric acid solution as before and deduction of any value corresponding with the chloroform-content, 1 c.c. of 0·05 *N* $AgNO_3 \equiv$ 2·76 mgrms. of chloral hydrate. J. G.

Devonshire Colic (Lead Poisoning) due to Cider. M. C. N. Jackson and L. N. Jackson. (*Lancet*, 1932, **223**, 717–719.)—The relation between this disease and the consumption of cider containing lead has been recognised since 1767, at which time much lead plant was used in the preparation of this beverage. In addition, the acidity of the product was "corrected" by the addition of metallic lead, litharge or lead acetate. A recent outbreak of Devonshire colic, involving ten cases (males), was traced to contamination of the cider supplied at six public-houses with lead in quantities varying from 1/10th to 1/20th grain per gallon. The cider in the casks in which it was delivered was free from lead, but, when received from the nozzles of the counter engines, contained the amounts recorded above. The source of the metal was the lead pipes connecting the casks and the engines, and similar results were obtained whether these pipes were tinned internally or not. As anticipated, the portions of cider which remained in the pipes overnight were most heavily contaminated. The analyses were carried out by destruction of the organic matter with sulphuric and nitric acids (*cf.* Wilkie, *J. Soc. Chem. Ind.*, 1909, 636), the determination being completed by the addition of sodium sulphide and comparison of the colour obtained with that yielded by known amounts of lead. T. J. W.

Agricultural

Determination of Cellulose in Soil. J. A. Daji. (*Biochem. J.*, 1932, **26**, 1275–1280.)—During the course of an investigation into the decomposition of green manures in soil it was necessary to determine the amount of cellulose that underwent changes at the different stages of fermentation. A method has, therefore, been devised, and is described for the determination of cellulose in soil mixed with plant materials. It is essentially a combination of the methods of Jenkins (*Biochem. J.*, 1930, **24**, 1428) and Charpentier (*Meddel. No.* 205, *Centr. Forsök. Jord. Bakter. Avdel.*, No. 22, 1920). The soil is treated with hot dilute alkali and acid, and then with a solution of sodium hypochlorite in the cold. Cellulose is then extracted from the residue with Schweitzer's reagent, precipitated with alcohol, and determined by loss of weight on ignition. The results obtained by this method on plant materials alone agree very closely with those given by the hypochlorite method of Jenkins. It is shown that it is necessary to remove the lignin from the plant tissues, otherwise it is not possible to obtain a quantitative yield of cellulose by extraction with Schweitzer's reagent. When different plant materials are mixed with soil, almost the whole of the cellulose added is recovered by the method, but a small part is retained by the soil, and is not extracted by the Schweitzer's reagent. This loss of cellulose was also observed by Charpentier and others, and was attributed by them to adsorption by the soil. No attempt has been made to apply the method to different types of soil. P. H. P.

Water Analysis

Determination of Hydrogen Sulphide in Industrial Waters. Kapp. (*Compt. rend.*, 1932, **195**, 608–610.)—Since at ordinary temperatures the oxygen dissolved in 1 litre of gas-washing water may oxidise about 18 mgrms. of hydrogen sulphide in 1 hour, or in less time if traces of iron are present, the iodimetric determination has been modified as follows:—To 500 c.c. of sample are added, as soon as possible, about 20 c.c. (an excess) of a 20 per cent. solution of cadmium sulphate; since the resulting cadmium sulphide is not appreciably oxidised, the analysis may be interrupted, *e.g.* for the sample to be taken from the works to the laboratory. The mixture is then heated to boiling in a flask provided with a tap-funnel and a delivery tube leading through a vertical coil-condenser into a known quantity of a solution of iodine, and 100 c.c. of a cool mixture of equal volumes of water and sulphuric acid are added slowly. Ten minutes after the disappearance of the colour of the sulphide the distillation is stopped, and the excess of iodine is titrated with sodium thiosulphate solution. If the sample is large (*e.g.* when the hydrogen sulphide content is small), the cadmium sulphide may be removed by filtration and added with the filter to 500 c.c. of water in the flask. J. G.

Organic Analysis

Determination of Fluorine and Boron in Organic Compounds. D. J. Pflaum and H. H. Wenzke. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 392–393.)—About 0·5 grm. of the substance is weighed in a gelatin capsule and placed in the cup of a Parr sulphur bomb of the electrical ignition type. A mixture of 10 grms. of sodium peroxide, 1 grm. of potassium chlorate and 0·5 grm. of sugar is added, the bomb is closed tightly, and the mixture is ignited. Pure iron wire is used for the fusion wire. The bomb is allowed to become quite hot, then cooled in water, opened, and the contents of the cup are dissolved in warm water. The solution is boiled and filtered, and the filtrate is boiled with the addition of 15 grms. of ammonium chloride until ammonia vapours are no longer evolved; this requires about two hours. The hot solution, filtered, if necessary, is treated with 10 c.c. of 2 *N* calcium nitrate solution and boiled, 1 c.c. of ammonia is added, the mixture is cooled, and the precipitate is collected on a filter, washed with water (not more than 50 c.c.), dried, ignited in a platinum crucible and weighed as CaF_2. Sufficient sodium hydroxide solution is added to the filtrate to produce a precipitate of calcium hydroxide and carbonate, the mixture is boiled until all ammonia is expelled, and filtered, and the filtrate is diluted to 250 c.c. Fifty c.c. of this solution are titrated with 0·1 *N* hydrochloric acid, methyl-orange being used as indicator; the remaining 200 c.c. of the solution are then neutralised by adding the requisite volume of 0·1 *N* hydrochloric acid, but no indicator; after the addition of mannitol and phenolphthalein solution, the mixture is titrated with 0·1 *N* sodium hydroxide solution, and the result is calculated in terms of boron. W. P. S.

Determination of Ethylene Oxide. O. F. Lubatti. (*J. Soc. Chem. Ind.*, 1932, **51**, 361–367.)—By means of Deckert's method of determining ethylene oxide, in which the oxide is converted into the chlorohydrin (*Z. anal. Chem.*, 1930, **82**, 297), it is not found possible to account for more than 94 per cent. of the oxide. When various modifications, particularly the use of magnesium chloride in place of sodium chloride, are introduced the method will, however, give results which are satisfactory and in agreement with those of Müller's dichromate method (*Chem.-Ztg.*, 1920, **44**, 573). The following modified form of this dichromate method is proposed: Use is made of a stout, thick-walled, flat-bottomed flask, holding about 400 c.c. and provided with a well-fitting ground-in stopper. The mouth of the flask expands into a flange for preventing loss of liquid during rinsing, and the stopper extends into a pointed tip to facilitate draining. Fifty c.c. of sulphuric acid (1:3) are pipetted into the reaction flask, which is left in a bath at 70° C. for 10 minutes and then removed. After the introduction of a tube of ethylene oxide (0·15 to 0·2 grm.), the flask is quickly stoppered, inverted and shaken until the tube is broken, and then shaken for 1 minute and allowed to cool slowly. After about 15 minutes, the stopper is removed and rinsed, and the open flask is again heated at 70° C. for 10 minutes, and afterwards cooled under the tap. With the help of a dry funnel, exactly 5·5720 grms. of "A.R." potassium dichromate (previously dried for 3 hours at 130° C.) are added, the funnel being rinsed with 25 c.c. of sulphuric acid (1 : 3) to remove adherent dichromate. The flask is heated gradually on a wire gauze over a small flame and kept gently boiling for 20 to 25 minutes, being swirled, at frequent regular intervals, to prevent loss by spurting. The liquid is then cooled to the laboratory temperature and made up to 500 c.c. with water in a measuring flask. Twenty-five c.c. of the solution, 400 c.c. of water, 25 c.c. of sulphuric acid (1 : 3), and 20 c.c. of 10 per cent. potassium iodide solution are introduced in order into a litre flask, the mixture being then titrated with thiosulphate solution (28·3 grms. per litre) in presence of starch. Concurrently with this determination, a blank without the oxide is carried out similarly. One c.c. of the dilute dichromate solution corresponds with 0·001 grm. of ethylene oxide.

When the modified Deckert method is employed for determining the ethylene oxide in a fumigated space, use is made of a special flask, devised by Page (*J. Soc. Chem. Ind.*, 1932, **51**, 369T). This flask, of 1-litre capacity, is fitted with a rubber stopper (covered with castor oil), carrying an exhaustion tube and a capillary gas-inlet, to which a small reservoir is attached inside the flask. Ten grms. of solid magnesium chloride ($+6H_2O$) and 50 c.c. of saturated magnesium chloride solution are introduced into the flask, and 5 c.c. of 0·5 *N* sulphuric acid into the reservoir. The stopper is inserted and the flask is evacuated, sealed, and tilted to allow the sulphuric acid to mix with the magnesium chloride solution. The gas-charge is then introduced, and the flask is well shaken for 30 seconds. The stopper with its fittings is well washed with 25 to 30 c.c. of water into a tall 150-c.c. beaker, the washings and the liquid in the flask being titrated together with 0·05 *N* sodium hydroxide solution in presence of methyl-orange; the first change to orange is taken as the end-point. A parallel test, without the gas containing ethylene oxide, is made in exactly the same manner: 1 c.c. of 0·05 *N* NaOH ≡ 2·202 mgrms. of C_2H_4O. T. H. P.

Test for Oxalic Acid. E. R. Caley. (*Ind. Eng. Chem., Anal. Ed.*, **1932, 4,** 445.)—A solution of 0·1 grm. of the acid in 2 c.c. of water is treated with 1 c.c. of 6 *N* sodium hydroxide solution and the mixture is shaken for two minutes. The formation of a white crystalline precipitate indicates oxalic acid. The following acids do not yield a precipitate, even when present in larger quantity than 0·1 grm.; citric, crotonic, glycollic, maleic, malic, malonic, mandelic, succinic, and tartaric. Dihydroxytartaric acid gives a precipitate in the test, but this acid is unstable and not readily obtained. W. P. S.

Essential Oil of *Dacrydium cupressinum*. M. S. Carrie. (*J. Soc. Chem. Ind.*, 1932, **51**, 367–368T.)—This oil, obtained by steam-distillation of the leaves and afterwards dried, was found to consist almost entirely of hydrocarbons, and to give three well-marked fractions when distilled under reduced pressure: (1) A terpene fraction (20 per cent.), consisting almost entirely of α-pinene; McDowall and Finlay (*ibid.*, 1925, **44**, 42T) found no terpenes. (2) A sesquiterpene fraction (9·4 per cent.), b.pt. 132 to 135° C./20 mm., sp.gr. 0·9238 at 20/20° C., n_D^{20} 1·5010 (1·4990 after two distillations over sodium), $[\alpha]_D + 17{\cdot}57°$; catalytic hydrogenation, using palladium as catalyst, shows that the compound is tricyclic, the double linking being probably in the nucleus. (3) A liquid diterpene fraction, giving as a well-marked sub-fraction (31 per cent. of the oil), a green, highly viscous oil, b.pt. 150 to 154° C./1 mm., sp.gr. 0·9763 at 15°/15° C., n_D^{15} 1·5211, $[\alpha]_D^{15} + 15{\cdot}17°$; hydrogenation and ozonolysis (which yielded formaldehyde) indicate the presence of 0·85 of a double linking in a side-chain, and it is assumed that the fraction represents a constant-boiling mixture of 85 per cent. of a tetracyclic diterpene with 15 per cent. of a saturated one. Only partial separation of these two was accomplished by fractionation of the hydrogenated product, and oxidation by permanganate of a waxy product formed, with the formaldehyde, on ozonolysis gave an acid of the probable formula $C_{14}H_{21}O.CO_2H$. McDowall and Finlay's solid diterpene, which was not found during the present examination, proves to be unsaturated, as it decolorises bromine in chloroform or absolute alcohol solution, although it does not do so in ether or carbon disulphide. T. H. P.

Chemical Examination of the Marking Nut. P. P. Pillay and S. Siddiqui. (*J. Indian Chem. Soc.*, 1931, **8**, 517–525.)—The black corrosive juice of the pericarp of the nut of the marking nut tree (*Semecarpus anacardium*, Linn.) is administered internally with emollient oils, and is of great medicinal value, besides being used in admixture with lime as an indelible marking ink. Anacardic acid, cardol, catechol and anacardol were not present, but the following substances were isolated from the black pericarp juice (of which 28 to 36 per cent. was obtained):—(1) "Semecarpol" a monohydroxyphenol boiling at 185–190° C. at 2·5 mm., solidifying below 25° C. to a fatty mass, and forming 0·1 per cent. of the extract; (2) "Bhilawanol," a *o*-dihydroxy compound, $C_{21}H_{32}O_2$, distilling at 225°–226° C. at 3 mm., solidifying below 5° C., and forming 46 per cent. of the juice; and (3) a tarry corrosive residue yielding no identifiable compound. Work on bhilawanol finally established the identity of the hydrogenation product, hydro-bhilawanol, with hydro-urushiol the hydrogenation product of uroshiol the chief constituent of Japan lacquer, the dried juice of *Rhus vernicifera*, and this parallel may eventually lead to the extension of the utility of each plant. The experimental work is described in detail. D. G. H.

Determination of Gum in Petrol. M. J. Mulligan, W. G. Lovell and T. A. Boyd. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 351–356.)—Fifty c.c. of the petrol are placed in a glass beaker fitted in a bath containing a liquid (*e.g.* ethylene glycol) boiling at about 200° C. Air flowing at the rate of 1 litre per second and heated by passing through a coil in the bath is used to evaporate the petrol and dry the residual gum. About twenty-five minutes are required to obtain a residue of gum of substantially constant weight. Oxidation during the evaporation and drying does not introduce appreciable error. W. P. S.

Inorganic Analysis

Use of Metallic Lithium in the Determination of Nitrogen, etc., in Inert Gases. J. H. Severyns, E. R. Wilkinson and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 371–373.)—A method for the determination of nitrogen, oxygen and water vapour in helium depends on the fact that metallic lithium forms non-volatile compounds with the impurities mentioned. The apparatus used consists of an inverted 400-c.c. round-bottomed flask fitted with three capillary taps which are sealed to the bottom of the flask; one leads to a manometer, another to a vacuum pump, and the third to the source of the gas sample. An electrical heating device, carrying a small iron boat is fitted into the flask by means of a glass tube and rubber stopper. A small piece of lithium is placed in the boat, the flask is exhausted, and the gas (helium) to be analysed is admitted slowly until the pressure reaches, say, 550 mm. Current is then supplied to the heating device, the lithium is melted, and rapid absorption of the oxygen and nitrogen takes place. Although water-vapour is also absorbed, this takes some time, and it is preferable to dry the helium previously. After about two minutes the heating is stopped and, when the apparatus is cold, the pressure is re-determined. The second pressure, divided by the first, gives the fractional purity of the sample. At ordinary temperature lithium does not react with oxygen, nitrogen or water-vapour within a period of five minutes. W. P. S.

Volumetric Analysis involving the use of Liquid Amalgams. S. Kaneko and C. Nemoto. (*J. Soc. Chem. Ind. Japan*, 1932, **35**, 343B.)—The following two simplified forms of Nakazono's method of volumetric analysis, in which liquid amalgams are used (*J. Chem. Soc. Japan*, 1921, **42**, 36), have been devised. (1) A portion of the sample solution, acidified with sulphuric acid and diluted to a known volume, is reduced by shaking for a few minutes in an 80-c.c. stoppered flask with 150 grms. of dry zinc, cadmium or bismuth amalgam, and 25 c.c. of the reduced solution are withdrawn and titrated with standard potassium permanganate solution. Amalgam for this purpose may be obtained in a dry condition from the stock of amalgam, which is ordinarily preserved under dilute sulphuric acid, by separation in the apparatus shown in Fig. 1, A and B being the outlets for dry amalgam and the acid preserving liquid respectively.

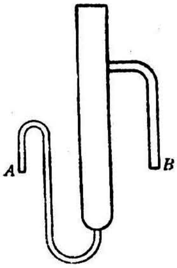


Fig. 1

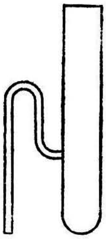


Fig. 2

(2) Twenty-five c.c. of the sample solution are shaken, as above, with 150 c.c. of the amalgam, which need not be dry. The whole is poured into an apparatus, as shown in Fig. 2, the aqueous liquid being received from the side tube in a separate vessel; the amalgam is well washed, the washings being similarly collected, and the combined liquids are titrated. S. G. C.

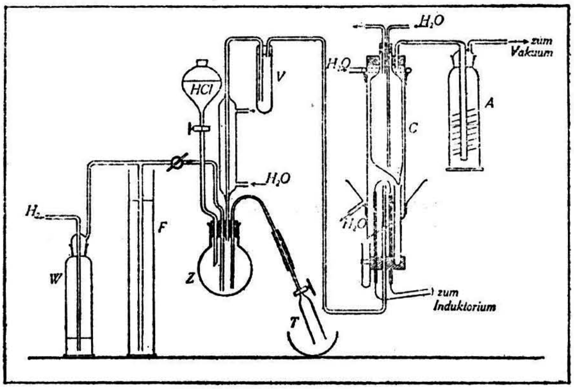
Determination of Antimony in Copper. H. Blumenthal. (*Z. anal. Chem.*, 1932, **90**, 118–121.)—A criticism of Boehm and Raetsch's paper (ANALYST, 1932, 538). It is observed that these authors added antimony in the form of a lead alloy to pure copper, the antimony being precipitated as lead antimonate when the nitric solution was treated with excess of ammonia. Quantitative recovery of the antimony was actually achieved without the use of iron, by adding 1·5 grm. of lead nitrate to the solution of 25 grms. of copper and precipitating with ammonia. In the analysis of bronze, the small amounts of antimony present are occluded in the relatively large precipitate of stannic acid; in the subsequent ammonia precipitation the ferric hydroxide present merely assists the filtration of the stannic acid. W. R. S.

Determination of Thallium after Oxidation with Bromine. E. Browning. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 417.)—Thallous salts are oxidised readily when their solutions are treated with a slight excess of bromine; subsequent

addition of ammonia causes precipitation of thallic hydroxide, which may be collected, dried at 150° to 200° C., and weighed. Qualitatively, 0·1 mgrm. of thallium in 10 c.c. of solution may be detected by the dark coloration of the thallic hydroxide.
W. P. S.

Rapid Colorimetric Determination of Nickel in Copper Alloys. V. P. Ochotin and A. P. Sytschoff. (*Z. anal. Chem.*, 1932, **90**, 109–111.)—The alloy (0·01 to 0·015 grm. for a 20 : 80 nickel-copper alloy) is dissolved in 10 c.c. of nitric acid, the solution is diluted to 25 c.c., and sufficient ammonia is added to convert the copper into the deep-blue ammine compound. The solution is treated with 15 c.c. of 1 per cent. dimethylglyoxime solution, and the liquid is cooled in a separating funnel and shaken with 15 c.c. of ether, which extracts the nickel precipitate, forming a suspension. The aqueous layer is removed, and the ether is washed twice with water and transferred to a colorimeter tube. After addition of 5 c.c. each of alcohol and of collodion to stabilise the suspension, the colour is matched against that obtained with a standardised sample. A determination can be made in 10 minutes. The suspension is stable for about 24 hours.
W. R. S.

Determination of Phosphorus in Aluminium. W. D. Treadwell and J. Hartnagel. (*Helv. Chim. Acta*, 1932, **15**, 1023–1029.)—A new micro-method is proposed by which as little as a few thousandths of one per cent. of phosphorus may be determined in aluminium or aluminium alloys. In outline, the aluminium is dissolved in acid in an atmosphere of hydrogen, and the phosphorus, liberated as phosphine with the hydrogen evolved, is oxidised by combustion, the phosphoric acid produced being collected and the phosphorus determined by the "molybdenum-blue" reaction. The apparatus required, which is shown in the diagram, is self-explanatory except for the combustion chamber, C. This is virtually a double-surface condenser, open at the bottom and consisting of an outer glass cylinder, about 25 cm. × 5 cm. in diameter, cooled by an external stream of water, and an internal vessel of special shape through which water is circulated. Projecting upwards into the combustion chamber are (*a*) the hydrogen leading tube, which terminates in a quartz capillary, 3 cm. × 0·5 mm. in diameter, to act as the burning jet; (*b*) platinum points connected to an induction coil, by means of the



sparks from which the issuing hydrogen is ignited in air which is drawn up, at a rate of about 1 litre per minute into the chamber, by means of the vacuum pump connected to A; two glass test-tubes are provided for collecting the condensed liquid from the two condensing surfaces. *Method.*—The sample of aluminium (0·1–1 grm., containing 1–60γ of phosphorus) is placed in the 100-c.c. decomposition flask, Z. Hydrogen is passed into the apparatus from a cylinder at about 160 c.c. per minute, as judged by the rate of bubbling in the water wash-bottle, W (the cylinder, F, is a pressure-regulator). The hydrogen is ignited, by sparking, at the quartz jet in C, and the height of the flame is adjusted to 6–8 mm. by regulating the admission of hydrogen into the apparatus. The solution of the sample in Z is effected by slowly dropping 10 per cent. hydrochloric acid from the dropping funnel at a rate so regulated that the dissolution occupies 20 to 40 minutes (the purpose of funnel, T, is to enable, if necessary, water to be introduced into the flask to reduce a possibly violent rate of solution, or exhausted acid to be withdrawn). Hydrogen is passed for 15 minutes after solution is complete, in order to sweep out the apparatus. The interior of the combustion chamber is finally rinsed out with water, and the condensate and washings, together with 1 or 2 drops of dilute sulphuric acid are evaporated in a platinum dish to a volume of about 10 c.c. The phosphorus-content of the liquid is determined by the "molybdenum-blue" method of Zinzadze (ANALYST, 1932, 411). It is stated that the phosphoric acid produced in the combustion of the phosphine is completely absorbed by the condensed water in the combustion chamber. S. G. C.

Separation of Beryllium from other Elements by Guanidine Carbonate. A. Jílek and J. Kota. (*Z. anal. Chem.*, 1932, **89**, 345–354.)—The method for the separation of beryllium from aluminium, described in an earlier paper (ANALYST, 1932, 406), can be used without modification for the separation of beryllium from ferric, uranyl, thorium, zirconium, copper, antimony, and thallium salts, and from chromic, molybdic, and arsenious acids. For the separation of beryllium from vanadic and tungstic acids, the weakly acid solution, after addition of the ammonium tartrate solution, should next be treated with a slight excess of caustic alkali, and then neutralised with dilute acid against methyl red. Guanidine carbonate reagent and formaldehyde are then added as in the original method. If this modification is not adopted, a little vanadic or tungstic acid finds its way into the beryllium precipitate. W. R. S.

Use of α-Benzoinoxime in the Determination of Molybdenum. H. B. Knowles. (*Bur. of Standards J. Research*, 1932, **9**, 1–7.)—α-Benzoinoxime, which has been proposed as a specific precipitating agent for copper in ammoniacal solution by Feigl (*Ber.*, 1923, **56**(ii), 2083), has been found to precipitate molybdenum quantitatively in acid solution and to provide a separation of molybdenum from many other elements. *General Method of Determination.*—The test solution should contain 10 c.c. of concentrated sulphuric acid and not more than 0·15 grm. of sexavalent molybdenum in 200 c.c. The solution is cooled to 5–10° C., and 5 c.c. of a 2 per cent. solution of α-benzoinoxime in alcohol for each 0·01 grm. of molybdenum present, with 10 c.c. extra, are added with stirring. Just sufficient bromine water to colour the solution a pale yellow is added, followed by a few c.c.

of the precipitating agent. The liquid is kept cooled 10–15 minutes, and is stirred occasionally. A little macerated filter-paper pulp is then stirred in, and the liquid is filtered through a filter-paper of close texture. The precipitate is washed with 200 c.c. of a cold, freshly-prepared solution containing 25 c.c. of the 2 per cent. alcoholic benzoinoxime solution and 10 c.c. of concentrated sulphuric acid per litre. The precipitate and paper are dried in a weighed platinum crucible, charred without flaming, ignited to constant weight at 500–525° C., and weighed as molybdenum trioxide. Good results were obtained in test experiments with 0·001 to 0·1 grm. of molybdenum present. The limits of the amount of reagent to be added would appear to be fairly critical, *viz.* from two to five times the theoretical (1 atom of molybdenum to 3 mols. of benzoinoxime), since incomplete precipitation resulted either (1) when slightly more than the theoretical or (2) when ten times the theoretical amount of reagent was used. Low results were obtained when the time specified for the precipitation was exceeded. Wide variations in the degree of acidity of the test solution are permissible, good results having been obtained, *e.g.* with solutions containing (*a*) acetic acid buffered with acetate, (*b*) up to 20 per cent. of sulphuric acid; solutions containing 5 per cent. of hydrochloric or nitric acid were successfully used when the presence of sulphuric acid was objectionable, *e.g.* in the presence of lead; phosphoric acid was found unobjectionable, but incomplete precipitation was obtained in presence of tartaric acid; hydrofluoric acid must be absent. A detailed survey of the behaviour of most other elements with the reagent indicated that the only elements besides molybdenum giving precipitates in mineral acid solutions are tungsten, palladium, sexavalent chromium and quinquevalent vanadium; tervalent chromium and quadrivalent vanadium cause no interference; niobium and silicon interfere by being partially precipitated with molybdenum.

The following applications of the method to commercial products were used by the author:

Molybdenum Steel.—One grm. was dissolved in 50 c.c. of dilute sulphuric acid (1 + 6) and oxidised with the minimum of nitric acid. The filtered solution was diluted to 100 c.c., and sufficient ferrous sulphate solution was added to reduce vanadic and chromic acids; it was cooled to 5–10° C., and the precipitation with α-benzoinoxime carried out as already described. The ignited oxide was examined for any "insoluble residue" and for tungsten. Test results cited of determinations of molybdenum in standardised chromium-molybdenum steels and in solutions of plain steel containing added molybdenum show fairly good agreement with the amount present. [*Abstractor's note:* The process would appear to be inapplicable, without modification, to steel containing much tungsten.]

Calcium molybdate, Wulfenite and Molybdenite Ore.—To the solution obtained by decomposing 0·2 to 0·5 grm. of the material with hydrochloric acid, or with nitric acid and bromine, followed by evaporating "to fumes" with 10–15 c.c. of sulphuric acid, dissolving the residue in 100 c.c. of water, and filtering (a small quantity of molybdenum was found in the insoluble residue by a colorimetric test made on the solution after fusing the residue with sodium carbonate), sufficient potassium permanganate was added to produce a permanent pink colour. Sulphurous acid was added to reduce any vanadic or chromic acid present, and the excess was removed by boiling. The benzoinoxime precipitation, as already described, was then carried out. The ignited and weighed impure molybdic oxide obtained was dissolved in the minimum of ammonia, and the insoluble residue was filtered off and ignited. The ammoniacal extract was acidified with hydrochloric acid, cinchonine was added to precipitate the tungsten present, and the liquid was kept overnight; the precipitate of cinchonine tungstate was then filtered off, washed, ignited at 525° C., and weighed. The weight of this tungstic oxide, together with that of the residue insoluble in ammonia, was deducted from the weight of the impure molybdic oxide. Good results were obtained in test experiments.

S. G. C.

Composite Reagent for Calcium. G. J. Cox and M. L. Dodds. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 361.)—The reagent is prepared by dissolving 200 grms. of crystallised oxalic acid and 500 grms. of ammonium chloride in 3500 c.c. of water, adding 1000 c.c. of glacial acetic acid and 10 c.c. of 0·04 per cent. methyl-red solution, and filtering the mixture. For the determination of calcium in bone-ash, or similar material, the ash is dissolved in dilute hydrochloric acid, a suitable quantity of the reagent is added, the mixture is boiled, and ammonia is added until the reaction is slightly alkaline to methyl-red. W. P. S.

Determination of Potassium as Chloroplatinate. R. Strebinger and H. Holzer. (*Z. anal. Chem.*, 1932, **90**, 81–86.)—The authors prove, in a series of tests, that alcohol containing acetaldehyde causes slightly low results in the determination of potassium as chloroplatinate, this being ascribed to partial reduction. Alcohol free from aldehyde is recommended. W. R. S.

Microchemical

Microchemical Reactions with Loretin. C. Van Zijp. (*Pharm. Weekblad*, 1932, **69**, 1191–1197.)—Loretin (2-iodo-1-hydroxyquinoline-4-sulphonic acid) is a stable reagent which gives highly anisotropic crystals with a number of metals, the microscopical characteristics of which sometimes allow the simultaneous detection of two different metallic salts. It is used medicinally in admixture with 20 per cent. of sodium bicarbonate ("yatren"). The ordinary technique of a drop-reaction is used, but in some cases it is necessary to hold the watch-glass containing the mixture over a vessel containing ammonia. Orange needles are obtained with barium and strontium carbonates, and with calcium phosphate, carbonate and chloride. Colourless needles (often radiating) are produced with sodium chloride, lithium carbonate (readily soluble in water), nickel and cadmium chlorides, copper acetate and sulphate, and also under certain conditions, with calcium and strontium carbonates (*vide supra*). Magnesium sulphate and oxide deposit slowly, on scraping the glass, highly anisotropic crystals having a principal angle of 74°, and similar to those obtained with zinc oxide, chloride and sulphate, and with manganese sulphate and carbonate. Ferrous sulphate and lactate give hexagonal crystals, whilst cobalt acetate gives a precipitate of indefinite structure. Mercurous, mercuric, potassium, ammonium, rubidium and caesium chlorides, magnesium, barium, calcium and strontium sulphates, iron salts, calcium oxalate, aluminium, bismuth and silver nitrates, lead acetate and carbonate, potassium antimonyl tartrate, zinc sulphide, uranyl acetate, sodium uranate and bismuth hydroxide give negative results. Applications to the detection of dolomite, of zinc in white lead, and of calcium in magnesium carbonate are described. J. G.

Chemical Identification of Foreign Substances in Metals and Alloys. M. Niessner. (*Mikrochem.*, 1932, **12**, 1–24.)—The "spot" methods of Feigl are used to identify foreign elements on metallic surfaces. An imprint of the surface is taken on gelatin paper, and the test is carried out on the paper. The metallic surface is first polished, and the impregnated gelatin paper (similar to that used in photography, and free from contamination), with a smooth surface, is placed on the metal and pressed down. The gelatin is impregnated with a suitable reagent, according to the element sought. In order to prevent drying of the gelatin paper, a piece of damp filter-paper, also impregnated with the reagent, is placed behind it. For very small pieces of metal the gelatin is mounted on a sheet of glass, and the metal is pressed on to the gelatin. The metal and gelatin paper should stay in close contact for 5 minutes. The paper is then carefully removed, and should show a mirror-image of the positions of the element in question on the metal. Where the colour has to be developed, as when the colour change takes place in alkaline solution, and the gelatin has been pressed to the metal while impregnated with acid solution, the paper should be immersed in the correct developer until the colour appears. When very acid solutions are necessary for the solution of the surface, stiff filter-paper must be substituted for gelatin paper. Examples of the detection of sulphur, of phosphorus, and of oxidising substances in iron and steel (with photomicrographs) are given, and the detection of copper, cobalt and nickel, separately, together, and in alloys, is described. J. W. B.

Application of Sodium Diethyldithiocarbamate Reaction to the Micro-Colorimetric Determination of Copper in Organic Substances. W. D. McFarlane. (*Biochem. J.*, 1932, **26**, 1022–1033.)—An examination of the reaction between copper and sodium diethyldithiocarbamate, discovered by Delépine (*Compt. rend.*, 1908, **146**, 981) and developed by Callan and Henderson (ANALYST, 1929, **54**, 650), was undertaken with the object of devising more accurate methods for the determination of copper in organic materials in studying the rôle of copper in metabolism. The examination has revealed certain points of importance in the quantitative application of the reaction: A. The golden-brown copper salt formed is much more soluble in amyl alcohol than in water. The coloured copper salt can be rapidly and quantitatively extracted from aqueous solution by amyl alcohol. The reaction may then be applied over a much wider range of copper concentration. B. The golden-brown colour is intensified in the organic solvent; thus the sensitivity of the reaction is increased. C. The depth of colour is directly proportional to the amount of copper present, provided that the range of copper concentrations is not too great. D. In alkaline solution, ferric pyrophosphate does not give the reaction, but the reactivity of the copper is unimpaired; therefore, in alkaline pyrophosphate solution copper may be determined in the presence of iron. E. The oxidation of cupric sulphide in the cold with saturated bromine water and 10 per cent. sulphuric acid does not interfere with the subsequent application of the colour reaction. These observations have been utilised in the development of procedures, by means of which copper may be accurately determined in biological materials. Blood, milk, liver, crude glutamic acid and crystalline haemoglobin have been analysed for copper, and the method used is described in each case. A sample of crystalline haemoglobin of unknown origin was found by the carbamate reagent to contain only 0·0057 mgrm. of copper per grm. of haemoglobin. P. H. P.

Electrical Micro-Determination of Mercury. F. Patat. (*Mikrochem.*, 1932, **11**, 16–21.)—The method, which is suitable for small amounts of mercury down to 0·15 mgrm., gives results which differ from the calculated amount by 0·004 mgrm. or less. Metallic mercury is dissolved in a small volume (0·5 to 2 c.c.) of concentrated nitric acid, and the solution is diluted to a suitable volume to give a strength of about 0·1 *N*; solutions as strong as 2 *N* may be used, but the mercury deposited is darker and more porous; dilute nitric acid solutions of mercury salts may also be used. An aliquot part of the solution is electrolysed by means of an apparatus adapted from that of Stock and Lux (*Z. angew. Chem.*, 1931, **44**, 200). The electrolysis is carried out in a narrow beaker having a capacity 8 to 20 c.c.; the mercury is deposited on the cathode, which is made of gold wire, 6 to 8 cm. long and 0·3 mm. thick, weighing 0·1 to 0·15 grm., whilst the anode is a small platinum spiral. The beaker is covered with a moist cover-glass to prevent loss by splashing. The potential should be 3 volts and the current is 0·015 to 0·080 amp., according to the acidity. The gas developed stirs the liquid. With a current of 0·25 amp. at room temperature electrolysis for at least 15 hours is necessary. When deposition is complete the cathode is removed without interrupting the current, washed by immersion in water, dried either for 3 hours over phosphorus pentoxide or for 24 hours over asbestos soaked in sulphuric acid, and weighed. For weights exceeding 0·9 mgrm. a longer cathode, twisted into a spiral, should be used. The cathode is cleaned by heating it over a very small flame. J. W. B.

Micro-Determination of Mercury. V. Majer. (*Mikrochem.*, 1932, **11**, 21–30.)—Mercury in amounts varying from 0·014 to 0·0001 mgrm. in a volume of 5 c.c. is determined by electrolysis. From a number of determinations of the amount of mercury left in solution after varying intervals of time, the deposition of mercury was found to follow a regular rule:—$\log s = \log s_0 - 0{\cdot}434\,Kt$, where s_0 is the original concentration of mercury in solution, and s that after time t. The constant, K, depends on temperature, rate of stirring, and surface of the vessel, and, in the conditions of the experiment, was found to be $4{\cdot}9 \times 10^{-2}$ min.$^{-1}$, and the deposition was 99 per cent. complete in 94 minutes, the temperature being 50° to 60° C. *Detail.*—The electrolysis-vessel consists of a test-tube, 110 mm. long and 8 to 8·5 mm. in diameter; this contains about 5 c.c. of solution (0·5 grm. of potassium chloride, mercury as mercuric chloride, one drop of approximately saturated ferrous sulphate solution, 0·1 c.c. of 0·5 per cent. copper sulphate solution, and two drops of 1 *N* sulphuric acid). The test-tube is immersed in a bath of known temperature, and the solution is stirred by small bubbles of carbon dioxide from a fine capillary dipping in the liquid; the carbon dioxide also prevents atmospheric oxidation. The mercury is deposited on a clean piece of iron wire, 110 mm. long, 0·4 mm. in diameter, placed in the solution. When chlorine is present in the test-solution, after the addition of 0·5 grm. of potassium chloride, clean air is passed through for 10 minutes; this removes all but about 10 per cent. of the chlorine, the last traces being removed by the ferrous sulphate. Sulphuric acid and copper sulphate, as before, are added, and the further procedure is the same; the iron wire is changed after each 30 minutes, and a further micro drop of copper sulphate is added. A total volume of up to 20 c.c. instead of 5 c.c. may be used, containing the same amount of mercury, but the constant K is then somewhat smaller. The weight of mercury deposited is calculated from the size of the drops of mercury distilled off from the iron wire. The wire is first dried for 15 minutes over phosphorus pentoxide, and is placed in a small distillation-tube drawn out to a capillary, 8 cm. long and less than 0·1 mm. in internal diameter. After distillation and centrifuging in alcohol the mercury usually forms a single drop which can easily be measured under the microscope. When several drops are formed it is necessary to place a cover-slip, etched with a numbered net-work (similar to Jörgensen's cover-slips) on the slide, so that the drops of mercury can be located and not confused with each other; they can be identified at 130 × magnification, and may be measured at 360 × magnification. The method has been used for the determination of mercury in the atmosphere.

J. W. B.

Rapid Determination of Small Amounts of Thallium in the Presence of Lead and Bismuth. F. Pavelka and H. Morth. (*Mikrochem.*, 1932, **11**, 30–33.)—A nephelometric method is used for the determination of amounts between 0·05 and 0·02 mgrm. of thallium; as much as 30 times the amount of bismuth and 50 times the amount of lead do not interfere; results are obtained with an error of the order of 2 or 3 per cent. *Detail.*—The test solution, which should contain 20 to 100γ of thallium per c.c., is treated with 2 or 3 drops of 1 : 1 nitric acid and 2 to 4 drops of 5 per cent. phosphomolybdic acid solution. After the liquid has stood for 5 minutes, and has been diluted to a suitable volume, such as 10 c.c., the turbidity is compared with that of a standard solution of thallium nitrate, containing 50 mgrms. of thallium per litre, which has been treated in the same way. The turbid precipitate formed cannot be filtered or centrifuged. Neither lead, bismuth, mercuric nor cadmium salts react with the reagent, but mercurous salts give a precipitate in dilute solutions of nitric acid, which dissolves on addition of further nitric acid. Potassium and ammonium salts should not be present. The turbidities were compared in an Autenrieth colorimeter; a Hahn colorimeter would also be suitable. J. W. B.

Micro-Detection of Aluminium. F. L. Hahn. (*Mikrochem.*, 1932, **11**, 33–36.)—The test for aluminium with 1,2,5,8-tetra-hydroxy-anthraquinone (quinalizarin) is more sensitive when carried out as a spot test than in a test-tube. The reagent reacts with magnesium in sodium hydroxide solution, giving a coloured precipitate. Beryllium can be precipitated from this solution in the presence of ammonium salts, whilst aluminium is precipitated in slightly acid solutions ($p_H = 5·4$ to $5·8$), so that magnesium does not interfere with the test. *Detail.*—Ten mgrms. of quinalizarin are dissolved in 2 c.c. of pyridine and diluted with

20 c.c. of acetone. Filter paper is treated with this solution and dried. The paper has the same lilac colour as light litmus paper, and turns red with acid and blue with alkali. When a drop of aluminium solution is placed on the paper the fleck appears bluer when held over ammonia, and redder when held over glacial acetic acid, than the surrounding paper. For aluminium alone the smallest amount detectable is $5 \times 10^{-3}\gamma$, and the limit of dilution is 5×10^{-7}. In the presence of 50,000 times the concentration of magnesium 1γ of aluminium in 1 c.c. can be detected. J. W. B.

Reviews.

THE BRITISH PHARMACOPOEIA, 1932. Published by Authority, under the Direction of the General Council of Medical Education and Registration of the United Kingdom. Pp. 50+713. London: Constable & Co., Ltd., 10–12, Orange Street, Leicester Square, W.C.2. September 30th, 1932. Price 21s. net.

A new Pharmacopoeia is often approached with mixed feelings, the hope that all the shortcomings of the previous edition will have been made good being coupled with the knowledge that an intimacy arising out of many years' companionship will be suddenly broken. The publishers have, however, done their best to create a most favourable first impression by the style in which they have issued the work, and the use of water-proof cloth for the cover will be a very great advantage in the case of a book which is destined for frequent use in the laboratory. The principal change in the format of the work is the use of small type for the characters and tests in the monographs; this change would appear to have been necessary to keep the work within reasonable dimensions, as it already runs to over 760 pages—an increase of 127 pages over the number in the revision of 1914.

The present revision of the Pharmacopoeia differs from its predecessors in that it has been prepared under the direction of a body, appointed by the General Medical Council on the advice of its Selection Committee, styled the Pharmacopoeia Commission, the general supervision of the work still being carried out by the Pharmacopoeia Committee of the General Medical Council. It was decided that the Commission should consist of a Chairman, three medical men, a pharmacognosist, a pharmacist, and an analytical chemist, together with a secretary. The actual work of sifting the mass of information available was carried out by six sub-committees appointed by the Commission, which sub-committees have in addition carried out a vast amount of work in deciding upon the most suitable tests and standards to be adopted. It is difficult to criticise seriously the constitution of these committees, consisting, as they do, entirely of those long and honourably known in their respective spheres; the addition of at least one other Public Analyst to the Pharmaceutical Chemistry Sub-Committee, however, might well be considered in the future.

The Pharmacopoeia Commission has attempted to produce a volume suitable for the whole British Commonwealth of Nations, but it has not included substances which have mainly a local use in particular parts of the Empire, as was done in the 1914 revision. It is anticipated that supplementary lists of substances may be issued under local laws in the particular parts of the Empire to which they refer. There is a precautionary legal note pointing out that in some parts of the Empire the Pharmacopoeia has statutory force, and also that there are local laws dealing with certain of the substances which are the subject of the monographs; an attempt has been made to mention all such cases, but it is to be understood that any direction of the Pharmacopoeia which is contradictory, or inconsistent with, the local law is deemed thereby to be superseded. It is hoped to publish complete future revisions at intervals of ten years, but it may be found expedient to issue supplements from time to time during the intervals of revision.

The International Agreement of 1930, to which His Majesty's Government subscribed with certain reservations, has been carefully considered during the compilation of the revised Pharmacopoeia. Of the 76 articles contained in the Agreement, 43 have been included in the Pharmacopoeia. Of these, 25 are in accord, whilst 18 differ in composition or strength. Of the 18, two are standardised on a different basis, 9 for which there are no standards in the Agreement are standardised in the Pharmacopoeia, whilst for 7 the standards given in the Pharmacopoeia differ, varying from half the amount in the Agreement (in four cases) to twice (in one case). With regard to the main general alterations which have taken place as a result of the present revision, it will be found that the list of additions comprises 128 articles, and the list of omissions 357 articles, whilst there are also 113 articles of which the names have been altered, 18 of which the composition has been altered, and 13 of which the strength has been altered.

It is reported that an arrangement has been made with the Pharmaceutical Society of Great Britain for all the omissions from the 1932 revision of the Pharmacopoeia to be described in the next edition of the British Pharmaceutical Codex.

Many preparations have been omitted on the score of redundancy or lack of therapeutic value. They are not considered further in this note, as the point is one of medical rather than analytical interest, but the following sentence from the Introduction is deemed of sufficient interest to quote: "The mere fact that a drug is frequently prescribed has not been a sufficient justification for its inclusion, and a number of drugs described in the last British Pharmacopoeia have been omitted on the ground of insufficient medicinal value." With regard to the question of the position of the Pharmacopoeia as a legal standard under the Food and Drugs (Adulteration) Act, the following quotation from "General Notices" is also of interest: "Substances or preparations so designated" (*i.e.* having the official titles as descriptions) "for use in medicine must conform to the requirements of the British Pharmacopoeia."

Molecular weights have been added for the first time; these are calculated to the first decimal place in most cases, although that of water is taken to the third. We are told that "The Tests for Identity are provided only as an aid to identification; they do not in every case suffice to establish proof of identity," but no indication is given as to whether this is due to the limitations of the present knowledge of analytical chemistry or to a desire to keep the monographs short.

The former of these alternatives is difficult to believe, and the latter would represent an undesirable state of affairs, as the obvious use of "Tests for Identity" is to identify the substance in question.

The general tests given in the appendix have been increased in number, and illustrations appear for the first time in the Pharmacopoeia. Some of the Qualitative Reactions given in Appendix V could have been extended with advantage. Thus the evolution of ammonia is to be recognised by the odour only, but the effect on litmus is much more sensitive, particularly to certain individuals. None of the various modifications of Denigès' test is given; neither is the persulphate test, nor the cobaltinitrite test for potassium, and there is no mention of any of the newer tests for the metals with organic precipitants. Many of these are specific and all are valuable, particularly as micro-methods.

The quantitative test for lead remains substantially the same, although the permissible limits have, in many cases, been reduced. The solutions to be tested are still directed to be filtered while alkaline, but in this case in the presence of ammonium acetate, since acetic acid is first added and subsequently neutralised by the addition of ammonia. The ammonium acetate appears to prevent that adsorption of lead on the filter paper, which takes place when alkaline solutions of lead are filtered. The method has been tried in the reviewer's laboratory with satisfactory results. The quantitative test for arsenic is also little changed, but the method of attaching the mercuric chloride paper is much improved. Many of the limits have been considerably reduced, and it is interesting to observe that in some cases, *e.g.* citric and tartaric acids and glucose, the limits given are lower than the one-hundredth of a grain per lb. (1·4 part per million) suggested by the Royal Commission on Arsenical Poisoning.

In addition to the tests for lead and arsenic, there are quantitative limit tests for chlorides, sulphates and iron. The addition of these tests is typical of the alterations made in connection with the tests for purity, which are generally more precisely defined. The phrase in the 1914 revision "shall not answer for the tests for . . ." no longer occurs, and in its place definite tests limiting the permissible amounts of impurities are laid down. In the determination of water-soluble ash, although it is directed that the ash shall be boiled with 25 ml. of water, the volume of the washing water is not specified. In ashes containing such salts as calcium sulphate the results obtained depend very largely on the amount of wash water used.

The strengths of many of the preparations (*e.g.* the acids and alkalis) are still given exactly, but the permissible limits are given in brackets immediately following. Thus acetic acid is stated to contain 33 per cent. w/w of real acid within the limits of 32·5 to 33·5. This is a great improvement and should do much to remove many uncertainties which have arisen in the past.

The description "Absolute alcohol" has been changed to "Dehydrated alcohol." To "dehydrate" surely means to deprive of water, and, as the strongest commercial alcohol is never either "absolute" or "deprived of water" in the limiting sense, there hardly seems sufficient reason to change such a well-known name.

The descriptions of some of the crude drugs are, at first sight, a little ambiguous. Thus, under Buchu, we find "It contains not more than 5 per cent. of the stems, and not more than 2 per cent. of other organic matter." Presumably what is meant is that 93 per cent. of the sample shall consist of Buchu leaves, but the use of the term "other organic matter" in this and other monographs appears to the reviewer to be rather unfortunate.

Alum, Borax and Cream of Tartar no longer have the prefix "purified," but there is a notice to the effect that the standards of the Pharmacopoeia do not necessarily apply to articles which are sold, under the same name, for other than medicinal use. This is a great improvement. Any Food and Drugs Inspector asking for "Purified Borax" immediately advertises his office, and yet there was always a difficulty in applying the Pharmacopoeial standards unless the exact Pharmacopoeial names had been used when purchasing.

Ergot is now standardised by means of the Van Urk-Smith colorimetric method. There are only two preparations—prepared ergot, which is powdered de-fatted ergot, and the liquid extract—both of which are standardised in a similar manner. It has, of course, been known for some years that the ergot preparations of the 1914 revision are valueless. There seems to be every reason to expect that this difficulty has definitely been overcome. No biological methods for the standardisation of ergot are suggested, although biological methods of standardisation are an important new feature of the work, these following, wherever possible, the Regulations made under the Therapeutic Substances Act, 1925.

Although many concentrated preparations have been on the market for a number of years, they have not previously been admitted to the Pharmacopoeia. On this occasion, however, eight concentrated infusions are described. There is, however, no concentrated infusion of digitalis, and it is expressly stated that for dispensing purposes fresh infusion of digitalis should be used, and this within twelve hours of its preparation.

The oil in crushed linseed is directed to be determined by extraction with ether. Petroleum spirit is now more usual.

Some preparations (*e.g.* solutions of ammonium acetate) are directed to be prepared to a given p_H, full directions for a suitable colorimetric process being given in one of the Appendices.

Interesting additions are such names as Lysol, Formalin and Aspirin, with the reservation that their use is limited to Great Britain and Northern Ireland, and that in those parts of the Empire where they are trade-marks they may be used only when applied to the products of the owners of the trade-marks.

The familiar specific gravity of ether (0·720) has now been altered to 0·720–0·724, which is probably more accurate, in spite of its unfamiliar appearance.

The names of the alcoholic solutions of simple substances have been altered from tinctures to liquors in accordance with the International agreement, although the former names are retained as synonyms; iodine and ammoniated quinine are popular examples. The medicated wines have all been omitted in accordance with the International Agreement. Ipecacuanha wine is replaced by a tincture of ipecacuanha having the same proportion of alkaloids. A slip inserted states that the tincture should be given in cases where the wine is called for, which suggests the possibility of the raising of some slight legal difficulties under the Food and Drugs (Adulteration) Act. Industrial methylated spirit is at last introduced, and is used in the preparation of 15 compounded articles, apart from its use in many instances in the preparation of reagents.

No material alteration is made in the names of magnesium oxide and magnesium carbonate, the former still being described as magnesia. Gregory's Powder, however, is now made from the carbonate, and not from the oxide, as formerly.

There is no question but that greater advances have been made and a greater number of improvements added than in any previous revision. All those who have given so freely of their time and their experience to the production of such a work are to be warmly thanked and heartily congratulated. The amount of work involved in the revision must have been enormous, but is justified by the results obtained. To all those either directly or indirectly interested in drugs, the work is, of course, indispensable, but every analyst will find it is of very great value as a work of reference in many different fields.

G. D. ELSDON

THE B.D.H. GUIDE TO THE B.P., 1932. Pp. xvi+122. London: The British Drug Houses, Ltd., Graham Street, City Road, N.1. 1932. Price 2s. 6d.

This volume can be heartily recommended as a handy and most useful guide to the 1932 revision of the British Pharmacopoeia. It is well printed on good paper and nicely bound in dark blue cloth, the only improvement that can be suggested in its general appearance being that its length might have been increased by about a quarter of an inch to make it uniform with the Pharmacopoeia itself.

The book consists of two parts: First, an introduction describing the main lines of difference between this revision and its forerunners; and, secondly, more detailed notes on each of the monographs now official. The plan has been adopted of placing a double black line at the extreme left hand of each note dealing with a substance which has been altered to a material extent, and a single black line against any note dealing with a substance which becomes official for the first time.

A vast amount of information has been condensed in an admirable manner, the minor alterations in purity or strength being all clearly expressed. The book cannot, of course, be used in any way as a substitute for the Pharmacopoeia; the intention of the publishers is that it should be used along with the new revision to facilitate comparison with the old; this rôle it will admirably fulfil.

G. D. ELSDON

CHEMICAL ENCYCLOPAEDIA. By C. T. KINGZETT, F.I.C. Fifth edition. Pp. viii+1014. London: Baillière, Tindall & Cox. 1932. Price 40s.

The demand for a volume of this description is evident from the fact that five editions have been published during the last thirteen years, and, in spite of rigorous condensation, the present one contains over 200 pages more than the previous edition. The text comprises a series of definitions and brief articles on a multitudinous selection of chemical subjects arranged in alphabetical order with, in many cases, references to scientific publications where further information may be obtained. Not only are the purely chemical terms for substances given, but also many trade names, and the author has wisely included references to some of the commoner physical phenomena. On the other hand, a small number of the subjects, such as "Labour in Industry," appear somewhat out of place in a work of this nature.

It would be impossible, in reviewing this volume, to check the whole of the data and references given, but an extensive investigation has failed to detect any error, either numerical or typographical, and the statements of fact are free from the serious errors too often encountered.

The whole volume is well produced, with legible text and excellent binding, and reflects great credit upon the author, whose patient and careful work has produced a work which will undoubtedly be in extensive demand and of considerable value to a wide circle of readers.

T. J. WARD

MAKERS OF CHEMISTRY. By ERIC JOHN HOLMYARD. Pp. xvi+314. Oxford: Clarendon Press. 1931. Price 7s. 6d. net.

If the justification of an author lie, as Sidney says of poetry, in his ability "to teach and to delight," then Dr. Holmyard, for one, has more than fulfilled his duty to his readers. In his latest book in the *Makers of Science* series he delightfully combines the two arts, so that our minds receive both entertainment and instruction at the same time. A skilful lapidary, he has culled the gems from many an ancient treasure-store, polished and cut them to his taste, and then displayed them anew in a setting of his own making. *Makers of Chemistry* is filled with data and anecdote nicely blended, which bear ample witness to the laborious and painstaking hours of study put in by the author. Primarily intended for the non-scientific reader, the book is written in a simple, lucid style that all may understand, with that happy choice of words for which Dr. Holmyard has become so justly famed. Insensibly the layman becomes interested in the chemical phenomena until, by the time the end is reached, he finds himself thinking in terms of chemistry. The book should prove a great boon to the average student of chemistry who does not wish to spend much time delving into many sources for a history of the subject, for here, clearly and concisely set out, is all he needs to know of the general lines of its development, "from its remote and obscure beginnings up to the establishment of the modern science by Dalton, Lavoisier, Avogadro, and their contemporaries." A special word of praise is due for the well-chosen illustrations, of which there are close on a hundred, of great interest in themselves.

Dr. Holmyard may congratulate himself on having admirably achieved his purpose, to enable "those with no special scientific training to understand how the great and fascinating science of chemistry slowly took shape, until at length it was set firmly upon its present fruitful course." *Makers of Chemistry* can but enhance the author's reputation, already widespread and always growing, as a writer of readable books.

M. NIERENSTEIN

Errata

Vol. LVII. 1932.

P. 337, line 23, *for* "69·30" *read* "3·465."

P. 377, third column of first table, *for* "Average error per cent." *read* "Average error per cent. in reading."

P. 570, line 20, *for* "Gallenkamp" *read* "Baird and Tatlock."

P. 571, line 7 from the bottom, *for* "acidity of" *read* "acidity and."

Milk Products Sub-Committee Report, No. 3.

P. 650, line 3 from bottom. Add to the reagents required: "2 *N* sodium hydroxide solution (approximate)."

P. 651. *For* "add *N*/2 sodium hydroxide solution" *read* "add the 2 *N* and, towards completion, *N*/2 sodium hydroxide solution."

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BRITISH ASSOCIATION
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(102nd YEAR)

YORK

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