

# THE ANALYST

THE ORGAN OF THE

## Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT  
OF ANALYTICAL CHEMISTRY

### Publication Committee :

E. RICHARDS BOLTON, F.I.C. (President).

L. K. BOSELEY, F.I.C.

A. CHASTON CHAPMAN, F.I.C., F.R.S.

CECIL H. CRIBB, B.Sc., F.I.C.

J. C. DRUMMOND, D.Sc., F.I.C.

J. T. DUNN, D.Sc., F.I.C.

BERNARD DYER, D.Sc., F.I.C.

E. B. HUGHES, M.Sc., F.I.C.

H. T. LEA, M.Sc., F.I.C.

P. A. ELLIS RICHARDS, F.I.C.

W. H. SIMMONS, B.Sc., F.I.C.

E. W. VOELCKER, A.R.S.M., F.I.C.

J. AUGUSTUS VOELCKER, M.A.,  
Ph.D., F.I.C.

Editor : C. AINSWORTH MITCHELL, M.A., F.I.C.

### Abstractors :

J. GRANT, M.Sc., A.I.C.

T. H. POPE, B.Sc., F.I.C.

D. G. HEWER, B.Sc.

P. H. PRICE, B.Sc.

R. F. INNES, F.I.C.

W. R. SCHOELLER, Ph.D.

W. P. SKERTCHLY, F.I.C.

---

---

VOL. LII.

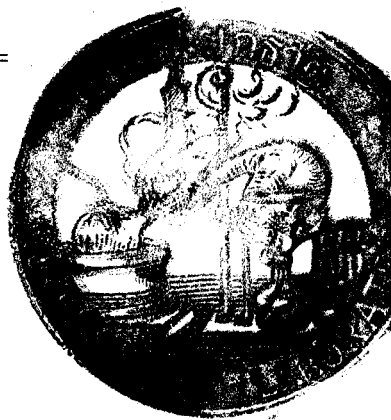
1927

---

---

PUBLISHED FOR THE SOCIETY BY  
W. HEFFER & SONS, LTD.  
4, PETTY CURY, CAMBRIDGE, ENGLAND

1927



# 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, December 1st, 1926, Mr. E. Richards Bolton, F.I.C., President, being in the chair.

Certificates were read for the first time in favour of Messrs. Solomon Greenberg, F.I.C., Frank Crafer Ray, M.A., F.I.C., and Geoffrey Charles Matthews, B.Sc., A.I.C.

A Certificate was read for the second time in favour of Mr. Stanley Grove Burgess, B.Sc., A.I.C.

The following were elected Members of the Society:—Miss Gertrude Garland Andrew, B.Sc., Messrs. Charles Edward Barrs, F.I.C., Thomas Hedley Barry, Gordon Watson Douglas, B.Sc., Clarence Victor Ferriss, B.Sc., A.I.C., and Reginald Charles Pakes, B.Sc.

The following papers were read and discussed:—"Recent Advances in the Bacteriological Methods of Examining Food and Water," by W. G. Savage, B.Sc., M.D.; "The Detection of Furfural in Vinegar," by L. H. Lampitt, D.Sc., F.I.C., E. B. Hughes, M.Sc., F.I.C., and L. H. Trace, B.Sc., A.I.C.; "The Rapid Determination of Opium in Stomach Contents," by E. R. Dovey, A.R.C.Sc., F.I.C.; and "A Rapid Method for the Sorting of Butters and Margarines," by C. H. Manley, M.A., F.I.C.

---

### Death.

With great regret we have to record the death of Sir William Tilden, Hon. Member of the Society, on December 9th, 1926. An Obituary will be published in a subsequent issue of the Journal.

## Potentiometric Titration of Tin with Potassium Bromate.

BY KARL SANDVED.

(Read at the Meeting, October 6, 1926.)

INTRODUCTION.—Of the numerous oxidising agents proposed for the titrimetric determination of tin, except for the two—iodine and ferric chloride—which are ordinarily used, potassium bromate appears to be the only one to have received serious attention. Györy (*Z. anal. Chem.*, 1893, **32**, 415) used potassium bromate in the volumetric determination of arsenic and antimony, and Zschokke (Fichte and Muller, *Chem. Ztg.*, 1913, **37**, 309) employed it to determine the strength of tin-baths used in dyeing in Basle. The appearance of a yellow coloration through the liberation of bromine marked the end-point, the ordinary dyestuff indicators being unstable in the presence of so strong a reducing agent as stannous chloride. The potassium bromate was standardised against pure tin under the same conditions as used during the analysis. A. Boller (*Diss.*, Zürich, 1915) has critically investigated this method, and has shown that it contains several sources of error. By adding potassium iodide and starch he found that the yellow colour of free bromine was visible only when an excess of bromate had been added, and that the results obtained were by no means reproducible. Referring to the earlier experiences of Fresenius (*Anleitung zur Quant. Analyse*, 1875, Vol. I, p. 364), Boller concluded that tin can be titrated accurately only when oxygen has been most rigorously excluded, for which purpose he employed a special apparatus, an excess of potassium bromate being added and re-titrated with potassium iodide and sodium thiosulphate. The titrations of Boller constitute, no doubt, the most exact work on this subject referred to in the literature, but, owing to its complexity and inconvenience, the method is not commonly used. Oesterheld and Honegger (*Helv. Chim. Acta*, 1919, **2**, 398) allege that these precautions are quite unnecessary when the bromate has been standardised against pure tin. Röhre (*Z. anal. Chem.*, 1924, **68**, 109) also found Boller's precautions to be superfluous if the titration was carried out as expeditiously as possible, a rough estimate of the amount of titrant required having previously been made.

Consequently, the only claim for these methods is that they will give reproducible results, the standardisation of the bromate against pure tin effecting the elimination of the constant errors. When one of the common analytical methods for determination of the bromate titre (arsenious oxide, thiosulphate, etc.) is used the results obtained are much too low, obviously owing to oxidation by the air. It seems very difficult to effect any improvement in the process of reduction, which takes place in an indifferent atmosphere, and in which the reducing agent and concentration of acid have been studied.

If a method could be found in which the oxidation by the air could be either eliminated or considerably reduced, it might be possible to use the same titre of potassium bromate for tin as for antimony or arsenic, instead of determining it for each particular metal. Thus Oesterheld and Honegger (*loc. cit.*) took advantage of the same titrating solution for antimony as for tin.

PRELIMINARY WORK.—Collenberg and Sandved (*Z. anorg. Chem.*, 1925, 149, 191) have used stannous chloride as a reducing agent for the potentiometric determination of iron with potassium bromate, and have shown that a sharp change in potential difference is obtained when the tin has been completely oxidised before the oxidation of divalent iron begins to take place. In the present work the potentiometric method is applied to the determination of tin. The original idea was to carry out the reduction directly in an indifferent atmosphere of carbon dioxide, and then immediately afterwards to titrate with potassium bromate without moving the beaker and without any addition of water. A convenient reducing agent must be chosen. Zinc and aluminium, which are usually used, proved quite unsatisfactory, due both to the vigorous liberation of hydrogen and to the slowness with which the precipitated tin re-dissolved. Attempts with titanous chloride and chromous chloride were also unsuccessful, as was to be presumed from the strongly negative stannic—stannous ion potential. At higher concentration of acid the oxidation of stannous ion took place before the oxidation of titanous ion. And with chromous chloride a constant hydrogen-potential was maintained at the electrode, owing to the slow reaction— $2\text{Cr}^{3+} + 2\text{H}^{+} \longrightarrow 2\text{Cr}^{2+} + \text{H}_2$ —which was catalysed at the platinum surface. By using the lead reductor according to Treadwell and Edelmann (*Helv. Chim. Acta*, 1922, 5, 806) the results obtained were 2 to 3 per cent. too low. The withdrawal of the reduced solution and the introduction of a process of washing out the reductor are not in agreement with the principles stated previously.

For several reasons metallic iron might be expected to be an efficient reducing agent; firstly, because it possesses the striking electro-chemical property of not precipitating tin from tin solutions (Kolthoff, *Chem. Weekbl.*, 1912, 16, 12; *Rec. trav. Chim. Pays Bas*, 1920, 39, 606; Bouman, *ibid.*, 537, 711); secondly, because the reduction is quantitative (A. Jilek, *Chem. Listy*, 17, 223, 268, 295); and, thirdly, because the compact iron gives a quiet liberation of hydrogen, which does not cause any splashing of the solution. The concentration of ferrous iron must, however, not be too great in order to obtain a fairly sharp inflexion after the oxidation of divalent tin is finished. As shown by Collenberg and Sandved (*loc. cit.*), some oxidation of the ferrous iron will take place before all stannous ions have disappeared, and the time necessary for obtaining constant potential is consequently dependent upon the velocity with which the ferric ions formed react with the stannous ions still present. If the concentration of ferrous iron becomes too large, oxidation of the iron will take place to a large extent, even on vigorous stirring, and the time thus required for establishment of the equilibrium of the system becomes too long. Some experiments which were carried out at 50° C., with the final volume 100 c.c., 50 c.c. of concentrated hydrochloric acid, and with

the use of flower wire in quantities varying from 0.25 to 1 gm., proved useless. A. Seuthe (*Mitt. Versuchsanstalt der Deutsch-Luxemburg Bergwerks u. Hütten A. G., Dortmund, 1924, 169-178*) states that the method of Finotti (*Chem. Ztg., 1922, 46, 1082*; Kolthoff and Heide, *Pharm. Weekbl., 54, 718*) gives correct values only when iodine and not bromate is used as the titrating solution. This result is best accounted for by the fact mentioned above.

The solution was therefore first reduced twice with 3 grms. of zinc in a long-necked Erlenmeyer flask, and then reduced with smaller quantities of iron in the titrating beaker. The results of a few titrations are given in Table I.

TABLE I.

No.	Reducing agent.	Temp. °C.	Conc. HCl. c.c.	Final volume. c.c.	Tin obtained. Grm.	Tin calculated. Grm.	Error. Per cent.
1.	1 × 3 grms. Zn. 0.055 grm. wire	50	50	100	0.0977	0.1008	-3.08
2.	2 × 3 grms. Zn. 0.055 grm. wire	"	"	"	0.1109	0.1139	-2.65
3.	"	"	"	"	0.1055	0.1087	-2.91
4.	"	"	"	"	0.0957	0.0981	-2.40
5.	"	"	"	"	0.1200	0.1231	-2.55

The bromate was standardised against pure sublimed arsenious oxide, and the titre of the stannous chloride solution used was found by electrolysis in oxalic acid, according to F. Henz (*Z. anorg. Chem., 1903, 37, 39*), as later described.

For comparison two titrations by the method of Oesterheld and Honegger (*loc. cit.*) and two by that of Röhre are given in Table II.

TABLE II.

No.	Method.	Tin obtained. Grm.	Tin calculated. Grm.	Error. Per cent.
6.	Oesterheld and Honegger .. ..	0.0737	0.0770	-4.28
7.	" " .. ..	0.0968	0.1008	-3.97
8.	Röhre .. ..	0.0746	0.0770	-3.11
9.	" .. ..	0.0974	0.1008	-3.37

As may be inferred from these data, the method does not offer any particular advantage over the methods used hitherto. The maximum deviation within the series is about 0.5 per cent., but the absolute values are 2.5 to 3.0 per cent. too low.

EXPERIMENTAL WORK.—After this preliminary work the method of titrating the tin directly with potassium bromate was abandoned. It seems to be the only safe way to add an oxidising agent in excess, but instead of re-titrating this excess, as is done by Boller, the author has found it better to titrate the reduction product formed. It is then quite unnecessary to know the concentration and the exact amount of the oxidising agent added, and the errors and complications due to a

re-titration are eliminated. F. Druce (*Chem. News*, **128**, 273) has employed the same principle, by using Knop's (*J. Amer. Chem. Soc.*, **46**, 263) excellent method for the titration of iron in the analysis of tin. In spite of the fact that diphenylamine may be used as an indicator for direct titration of tin with potassium bromate, Druce prefers a preliminary oxidation with ferric chloride.

A solution of tin ("Kahlbaum in Blöcken") in hydrochloric acid was prepared. The metal was analysed by the method of E. Victor (*Chem. Ztg.*, 1905, **29**, 179), and showed only traces of impurities. The solution was measured from a burette, and the contents of tin determined by Henz's method. Potassium bromate (*pro analysi*) was re-crystallised, dried at 125° C., weighed and dissolved in boiled distilled water in an atmosphere of carbon dioxide. The titre of the potassium bromate was found by means of freshly sublimed arsenious oxide according to Györy's method (*loc. cit.*), and potentiometrically by the method of Zintl and Wattenberg (*Ber.*, 1923, **56**, 472). The results obtained agreed well with each other.

The reduction was carried out in a 500 c.c. round-bottomed flask with a long neck, which was covered with a funnel, through which was passed a narrow glass tube for the introduction of the carbon dioxide. After the addition of 20 c.c. of concentrated hydrochloric acid, the reduction was started with 3 grms. of zinc "Kahlbaum," rods 3 mm. in diameter. This operation was repeated three times, 3 grms. of zinc and 20 c.c. of concentrated hydrochloric acid being added each time. Before each addition complete solution of the precipitated tin was obtained by boiling the liquid. Zinc proved here the most useful reducing agent, this metal—as was also shown by blank tests—being quite free from disturbing impurities. Aluminium has, besides the troublesome frothing on solution in acid, the disadvantage of always containing iron, for which in this case a special correction must be made. L. Smith (*Z. anal. Chem.*, 1922, **61**, 113) states that the efficiency of the reduction depends to a large extent on the concentration of free acid; both too rapid and too slow solution of the metal leads to incomplete reduction. When using aluminium he found it convenient to work with 55 c.c. of concentrated hydrochloric acid in 100 c.c. of solution. The velocity of solution depends, however, not only upon the temperature and degree of acidification, but also upon the form of the metal used, and by using so compact metal as zinc rods, 3 mm. in diameter, the author has found it advantageous to add greater quantities of acid, as described above. The zinc turnings used by Oesterheld and Honegger are useless in this method on account of their great velocity of solution. Moreover, these turnings have, as mentioned by Owe (*Tidsskrift for Kemi og Bergvosen*, Oslo, Norway, 1923, **3**, 9), a troublesome tendency to adhere to the neck of the flask. It is of essential importance for the efficiency of the method to use as high concentrations of free acid as possible, for it will cause the tin which separates to dissolve more rapidly, and it is just this operation, carried out in three stages, which requires the longest time, and thus in reality detracts from the ease with which the method can be carried out. A high concentration of acid will also secure a rapid reaction with the oxidising agent subsequently added. Smith's

experience that tin precipitated in cold solution dissolves more rapidly than tin separated from hot solution agrees with the author's observations. Zinc is therefore always added to cold solutions, and heating only resorted to when the spongy tin has been floating quietly on the surface without any liberation of gas. Jilek (*loc. cit.*) states that zinc in solutions of hydrochloric acid reduces incompletely and variably. Under the conditions just described this is not my experience.

By means of a special test for determining the concentration of free acid the solution, after reduction was complete, was found to contain 20 to 25 c.c. of concentrated hydrochloric acid per 100 c.c. of solution. For the subsequent titration with potassium bromate it was found convenient to use a titration volume of about 150 c.c. (Collenberg and Sandved, *loc. cit.*).

In order to test the reduction after each addition of zinc, determinations were made after the first, the second and the third addition, each on three grms. For analysis the ferric chloride method was used, as later described. As stated by Oesterheld and Honegger (*loc. cit.*) and Owe (*loc. cit.*), among others, it is absolutely necessary to carry out a repeated reduction, because the zinc pieces are covered with a layer of tin sponge which protects the free reducing surface. Table III shows that a single reduction is insufficient, and also that after two such reductions there still remains 0.6 per cent. before the lower limit is reached.

TABLE III.

No.	Zinc added	Tin obtained.	Tin calculated.	Error.
	(diameter, 3 mm.). Grms.			
10.	1 × 3	0.0651	0.0770	- 15.45
11.	2 × 3	0.0761	0.0770	- 1.17
12.	3 × 3	0.0766	0.0770	- 0.52

ATTEMPTS WITH PENTAVALENT ARSENIC.—A solution of disodium arsenate was added to the solution of stannous chloride in quantities varying from two to three times the stoichiometric amounts, but no trace of trivalent arsenic could be observed, even after boiling for thirty minutes. On boiling in hydrochloric acid (25 per cent.) metallic arsenic separated, as was also observed by Bettendorf (*Z. anal. Chem.*, 1870, 9, 105). At this temperature, however, arsenic chloride is considerably volatile. The method is therefore inapplicable under all conditions, owing to the remarkable resistance of the pentavalent arsenic to the action of reducing agents (Nissenson and Mittasch, *Chem. Ztg.*, 28, 184; Zintl and Wattenberg, *loc. cit.*).

ATTEMPTS WITH PENTAVALENT ANTIMONY.—A *M*/10 solution of potassium pyroantimonate,  $K_2H_2Sb_2O_7$ , was used as the initial material. The pentavalent antimony was added in quantities from 2 to 2.5 times the stoichiometric amounts. The solution was boiled just before the addition, in order to prevent access of air. The addition was carried out by pouring the solution from a 50 c.c. Erlenmeyer flask through the funnel fitting into the round-bottomed flask, as previously described. Carbon dioxide was passed through the flask during this operation, and

TABLE IV.

No.	Conditions of oxidation.	Tin obtained. Grm.	Tin calculated. Grm.	Error. Per cent.
13.	5M at 80° C. Cooled before being poured out .. ..	0.0762	0.0770	-1.04
14.	5M at 80° C. No cooling before pouring out .. ..	0.0763	0.0770	- 0.91
15.	5M at 50° C. .. ..	0.0998	0.1008	- 0.99
16.	15M at 50° C. .. ..	0.1000	0.1008	- 0.79
17.	5M at 65° C. .. ..	0.1240	0.1253	- 1.04
18.	Direct addition without cooling ..	0.0561	0.0770	-27.20
19.	" " " " ..	0.0781	0.1008	-22.60
20.	" " " " ..	0.0834	0.1008	-17.30

after the reaction was finished, the solution was transferred to a 400 c.c. beaker and made up to about 150 c.c. Under these conditions the concentration of acid is about 15 c.c. of concentrated hydrochloric acid in 100 c.c. The titration with potassium bromate was carried out potentiometrically by the method of Zintl and Wattenberg (*loc. cit.*). This method is less dependent on the concentration of acid and amount of titrating substance than is the original method of Györy (*loc. cit.*), in which ordinary dyestuff indicators, such as methyl-orange, are used. As shown by O. Collenberg (*Tidsskrift for Kemi og Bergvoesen*, Oslo, Norway, 1925, 5, 220), the two factors mentioned above are of essential importance in the discoloration of the indicator, and a fading in the colour of the indicator towards the end-point was also observed in many cases.

The titrations were all carried out by using the ordinary mono-metallic electrode system. A piece of smooth platinum foil, 19 sq. cm., functioned as an indicator electrode, and a *N* calomel electrode as an auxiliary electrode. A capillary electrometer was used as a zero instrument, and the P.D.'s were measured by the Poggenдорff-Ostwald compensation method.

As may be seen from Table IV, the titrations up to No. 18 agree well, but are a little too low, the average error being about 0.9 per cent. This, however, is a distinct advance on the results obtained by direct titration, in which the error varied from 2.5 to 3.0 per cent. The second column shows the conditions under which the oxidation was effected, *viz.*, the temperature and the time taken for the reaction between divalent tin and pentavalent antimony. The reaction was complete at 50° C. in 5 minutes, and raising the temperature to 80° C. did not cause any alterations in the result. At these temperatures it does not seem of any importance to cool the solution before transference to the titration beaker. It may, however, be seen from the three last experiments that the values obtained by adding the potassium pyroantimonate directly to the reduced solution immediately after heating are much too low. By cooling the solution before pouring it into the titration beaker the loss may be diminished, but is still about 17 per cent. (No. 20). The boiling point of the solution was found to lie at about 120° C. In Plato's method (*Z. anorg. Chem.*, 1906, 68, 33) the antimonous chloride is distilled off at a



temperature of 155° to 165° C. These titrations seem to show that the antimonous chloride formed in strong solutions of hydrochloric acid when subjected to a current of carbon dioxide is considerably volatile at lower temperatures. It is, therefore, absolutely necessary to cool the solution before titration with potassium bromate.

It seems, however, that the deficit of 0.9 per cent. cannot be due merely to incomplete reduction, for the titrations with ferric chloride, to be described later, show that the error may be rendered still smaller.

The reaction between pentavalent antimony and divalent tin is very slow, much slower than the corresponding reaction between ferric ion and stannous ion. Zintl and Wattenberg (*loc. cit.*) have shown that it is impossible to obtain a sharp break of the curve by potentiometric titration of a mixture of stannous salts and antimonous salts with potassium bromate, because the pentavalent antimony formed just before the end-point does not react sufficiently rapidly with the stannous tin still present.\* Pinkhof (*Diss.*, Amsterdam, 1919) has shown that this reaction is catalysed by iodide ions, but obviously this fact can not be made use of here.

TITRATIONS WITH TRIVALENT IRON.—A boiled solution of ferric chloride in hydrochloric acid was added in quantities from 2 to 2.5 times the stoichiometrically calculated amounts. It was found that the ferric chloride could be added to the boiling solution of stannous chloride without any loss, this being a great advantage compared with the method previously described. Hence oxidation by the air should be unlikely. After transference of the solution to a 400 c.c. beaker and dilution of the solution to about 130 c.c. the titration was carried out at 50° C., as described by Collenberg and Sandved (*loc. cit.*). Eight c.c. of a 0.25 molar solution of cobaltous chloride was added as a catalyst.

TABLE V.

No.	Tin obtained. Grm.	Tin calculated. Grm.	Error. Per cent.
21.	0.0767	0.0770	-0.39
22.	0.1003	0.1008	-0.50
23.	0.1137	0.1142	-0.44
24.	0.1248	0.1253	-0.40
25.	0.1364	0.1371	-0.51
26.	0.0766	0.0770	-0.52
27.	0.1003	0.1008	-0.50

Table V gives the results of a few titrations by this method. The measurements were made by using the common mono-metallic electrode system, as

\* M. Fleysher (*J. Amer. Chem. Soc.*, 1924, 46, 2725) states, however, that he has obtained a good break by using potassium dichromate as a titrating solution, but he has not given any exact information as to the time required for establishing constant potentials. This highly interesting fact does not seem to be due to an increased velocity of the oxidation of tin, this velocity also being fairly high when potassium bromate is used. The reason is probably a special catalysis of the secondary reaction mentioned above. Fleysher has adopted the method for the simultaneous determination of antimony and tin in the same solution. It seems to the author, however, that a simultaneous titration of antimony and tin can hardly claim any analytical importance, because a method for the quantitative reduction of tin without causing precipitation of metallic antimony is hitherto unknown.

previously described. The table shows that the concordance is very good, and that the deviation from the correct values has been reduced to 0.4 to 0.5 per cent. This limit is apparently very difficult to pass, owing, possibly, to incompleteness of the reduction process itself. Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, 41, 1337) found that the formation of ferrous iron takes place to some extent when an aqueous solution of ferric chloride is boiled. This does not appear to be the case if hydrochloric acid is added to prevent any precipitation.

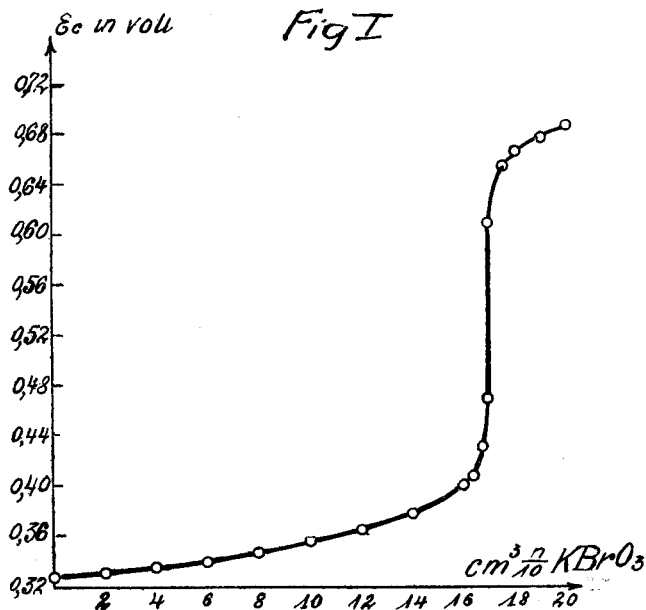
In working out the method for application to the common antimony and tin alloys several titrations were made after adding trivalent antimony to the solution. It seems advisable to remove the metallic antimony precipitated by the first reduction from the solution by a special filtration—an operation which requires only a short time compared with that necessary for the process of reduction. Hence this operation does not materially complicate the method, but permits, on the other hand, of an exact tin determination, in which the real titre of the potassium bromate may be used. In order to obtain a quantitative separation of the antimony by the first reduction it has been found necessary to effect the reduction in a special way. The first addition of zinc was increased from 3 to 4 grms. and added in portions of 2, 1 and 1 gm. The reduction was carried out in cold solution, and the next portion not added until the previous one was completely dissolved. It was necessary to use zinc with greater surface, and therefore turnings from zinc rods were used. These turnings dissolved rapidly, and the whole process took only a short time. After the solution of the last quantity of zinc 10 c.c. of concentrated hydrochloric acid were added, and the solution boiled until all tin was dissolved. The solution was then filtered through a small asbestos filter into a new round-bottomed flask, filled with carbon dioxide, and the filter was washed with hot hydrochloric acid (1:1). The filtrate was then reduced with zinc rods, 3 mm. in diameter, added in two portions of 3 and 2 grms. In Table VI are given the results of three titrations in which different quantities of antimony but the same quantity of tin were used. By using these quantities of antimony and tin the error has never exceeded -0.70 per cent.

TABLE VI.

No.	Molec. proportion between antimony and tin.	Tin obtained. Grm.	Tin calculated. Grm.	Error. Per cent.
28.	1	0.1003	0.1008	-0.50
29.	2	0.1001	0.1008	-0.69
30.	3	0.1002	0.1008	-0.60

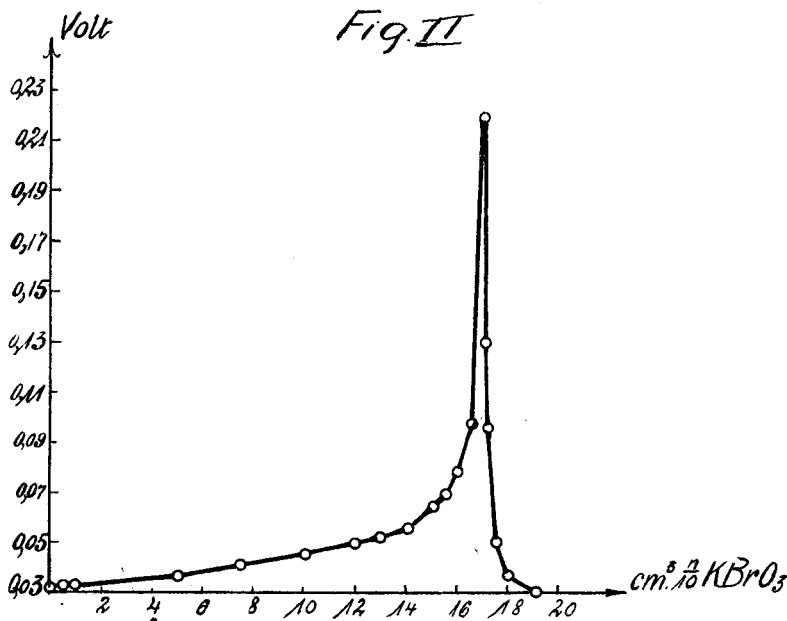
EXPERIMENTS WITH DIFFERENT ELECTRODE SYSTEMS.—All the titrations just mentioned were made by means of the common mono-metallic system, as previously described. Fig. 1 gives a typical curve obtained by using this system. The high electrolyte concentration, due to the great quantities of zinc added, gave rise to a considerable diminution of the potential difference in the region of the inflexion. Thus Collenberg and Sandved found a P.D. of 670 millivolts by using 15 c.c. of

concentrated hydrochloric acid to 100 c.c. of solution. Nor was this value materially altered by varying the concentration of hydrochloric acid from 10 to 20 c.c. per 100 c.c. of solution. With this method the point of inflexion lies at about 580 millivolts. In this range of electrolyte concentration the apparent activity coefficient of the higher charged ferric-ion consequently falls more rapidly with increasing "ion-concentration" than does the activity coefficient of the ferrous ion (Bjerrum, *Z. anorg. Chem.*, 1920, **109**, 275).

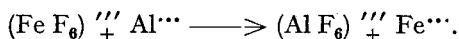


The bimetallic electrode system adopted by Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 4504) is, as was shown by Collenberg and Sandved, applicable in the titration of iron with potassium bromate. In Fig. 2 is shown an example of a titration curve obtained with this system. Two platinum wires of 0.4 mm. in diameter, polarised by a current of  $0.8 \times 10^{-5}$  amp., were used as electrodes. The shape of the curve seems to indicate that this electrode possesses a high reversibility on both sides of the inflexion point (Van Name and Fenwick, *J. Amer. Chem. Soc.*, 1925, **47**, 19). The free bromine formed when potassium bromate is added in excess acts as an effective cathodic depolariser. For the titration of manganese by the method of Müller (*Z. anorg. Chem.*, 1923, **129**, 35) Sandved and Backer (*Tidsskrift for Kemi og Bergvoesen*, 1925, **5**, 224) have introduced a bimetallic system consisting of a platinum shell and a platinum wire without any outer polarisation circuit. It is evident that by using such a system the reversibility of the electrodes is of more fundamental importance than by the method of Willard and Fenwick, the whole effect being here based upon polarisation within the system itself. Van Name and Fenwick (*loc. cit.*) found that the chief factor which determines

the sharpness of the electrometric end-point with polarised electrodes of pure platinum is the difference in the degree of reversibility of the electrode reaction before and after the end-point, and that the more nearly the electrode reactions conform to the requirements of complete reversibility on the one side of the end-point and of complete irreversibility on the other, the more distinct will be the end-point inflexion. Acting in accordance with this statement, the author has added polarisers to the system, in order to render the method mentioned



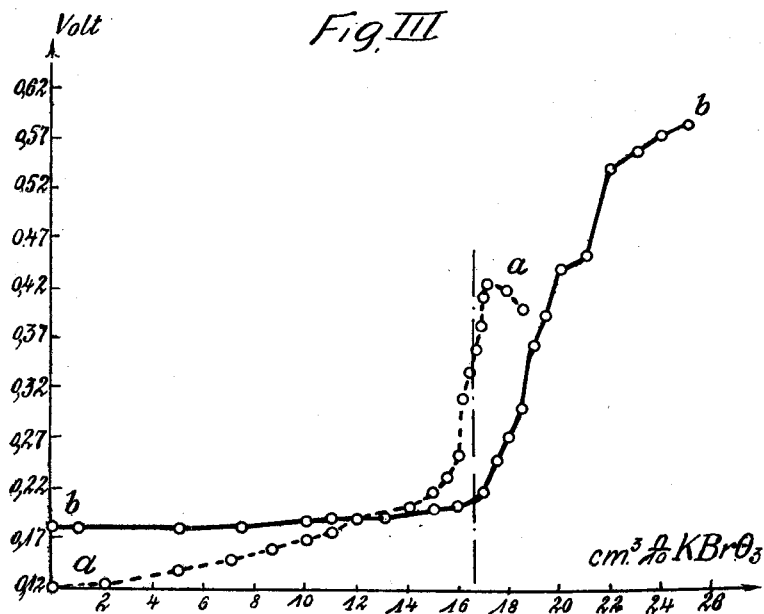
available for the present case. Potassium fluoride has been tried as a polariser, the fluoride ion forming a very strong complex ion with the ferric ion, which does not affect the ferrous ion (Treadwell and Köhl, *Helv. Chim. Acta*, 1925, 8, 570). An effect was observed, but the time required for the electrodes to re-assume the same potential was too short to render the method of any analytical utility. On adding aluminium ions in excess the effect disappeared, the ferric ion being liberated:



These facts seem to afford an excellent illustration of the extended reversibility of the ferrous-ferric electrode.

The platinum wires assumed quite striking electro-chemical properties after being dipped into hot hydrofluoric acid for some time. In Fig. 3 is shown a curve obtained by using this electrode. The dotted curve *A* is that obtained in a bi-metallic electrode titration, according to Willard and Fenwick, by using one attacked and one unattacked platinum wire, and the continuous curve *B* represents

the ordinary mono-metallic titration by measuring the potentials of the attacked platinum wire against the constant half-cell. The vertical line gives the calculated amount of potassium bromate. The curves, besides being very irregular in their shape, are dislocated towards the right. Apparently the electrode does not react at the true inflexion point, but requires an excess of oxidising agent to change it from its passive state. Moreover, the electrode retained these properties on ignition and treatment with strong acids. Before being immersed in hydrofluoric acid it

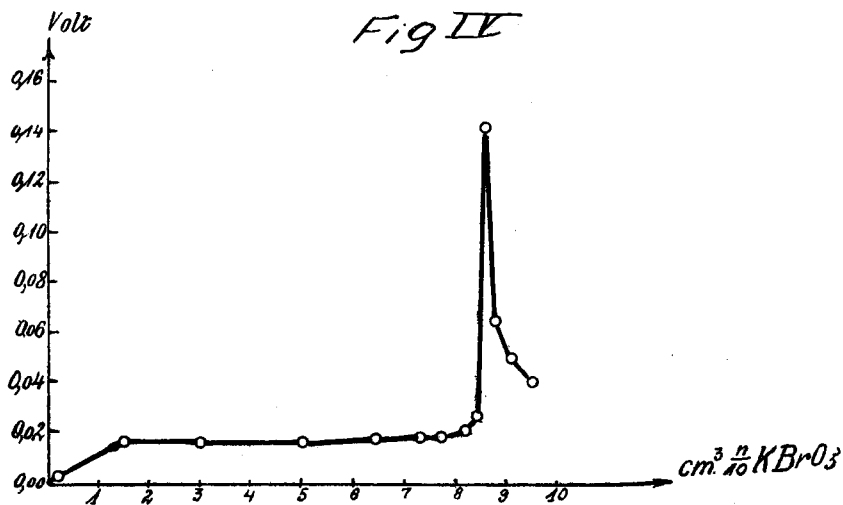


worked very satisfactorily. In their work on potentiometric determination of iron with potassium dichromate Hostetter and Roberts (*loc. cit.*) have examined the influence of different electrode materials. A palladium electrode, measured against the calomel electrode, gave no inflexion at all, and hence the authors concluded that the palladium metal was attacked by the electrolyte, and consequently displayed an approximate constant potential. The platinum electrode used here seems to behave as a partly attacked electrode, functioning as a Hostetter-Roberts palladium electrode until a little past the stoichiometrical changing point, whilst the subsequent curve tends towards the normal shape. In order to be independent of all disturbing effects, all electrode material used in titrations in which the bimetallic system is employed should be tested against one of the standard half-cells.

D. C. Cox (*J. Amer. Chem. Soc.*, 1925, 47, 2138) has recently adopted for some alkalimetric and acidimetric titrations a new system called "Differential electro-titration," in which the solution is divided into two equal parts in two beakers. An unattackable electrode is immersed in each beaker, and the two solutions are

connected electrolytically by a wet strip of filter paper. Two burettes are used for the titration, one for each beaker, and the titration is carried out in such a way that the amount of titrant added from one burette is a little greater (about 0.2 c.c.) than the amount added from the other. The E.M.F. of the cell thus formed becomes a maximum at the stoichiometrical end-point, and the amount of titration solution added is found by addition of the readings on both burettes.

Fig. 4 is a curve obtained by applying the method of Cox to the present system. Cox emphasises the advantages of eliminating all diffusion potentials and all erratic potentials at the electrode. These factors seem to the author to



be of little value, the absolute potential values being of no importance in a potentiometric titration with the bimetallic system. The complication which is introduced by using two burettes and two solutions more than counterbalances the simplification obtained by omitting the calomel electrode. The advantages which Cox claims are common to all forms of the bimetallic system. On the other hand, the author has found it convenient to apply a similar method for carrying out two parallel titrations. One sample was most simply titrated against the other as a constant half-cell until an ordinary inflexion point was obtained; and afterwards the second sample was titrated until the whole cell thus formed gave an E.M.F. equal to zero. In this way excellent results have always been obtained. The method in this form, however, denotes only a special application of the inflexion electrode, introduced by Treadwell and Pinkhof (E. Müller, *Die Elektrometrische Massanalyse*, p. 73).

**SUMMARY.**—The advantages of the indirect methods for titrimetric estimation of tin are shown.

A method based on that of Collenberg and Sandved for the determination of iron with potassium bromate has been worked out for the titration of tin; this

involves an initial oxidation of divalent tin with trivalent iron, and the subsequent titration of the ferrous iron formed with potassium bromate. This method eliminates the difficulties and complications of the method of Boller. The application of the method to the determination of tin in presence of antimony is also described.

The action of pentavalent arsenic and antimony on stannous salts has been investigated, and the quantitative reduction of the stannic salts is discussed.

Different electrode systems for the potentiometric titration of ferrous iron, formed in the process, with potassium bromate have been examined, and new points on the reversibility of the ferric-ferrous-electrode have been elucidated.

The author takes this opportunity of thanking Professor O. Collenberg, Lund, for valuable advice in carrying out this work, and also Dr. H. T. S. Britton for correcting the English translation of his paper.

The work was carried out with the assistance of a grant from the Research Fund of the Norwegian Technical High School.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
LONDON.

#### DISCUSSION.

Dr. EVANS said that he was surprised at the author's inability to get complete reduction of tin with lead, especially in view of the fact that an atmosphere of carbon dioxide was used throughout; he was in the habit of using an unpublished method of his own, wherein the tin was reduced by boiling the solution, strongly acid with hydrochloric acid, with a coil of lead in an atmosphere of carbon dioxide for one hour, and then driving the liquid over into a reagent containing, *inter alia*, a measured excess of iodine, and finally back-titrating. This method gave theoretical results on known amounts of tin; that is to say, the iodine need not be standardised against tin (as was usually done), but the correct normality could be used in the calculation; this showed that tin could be completely reduced by lead. He had tried nickel reduction and found it unreliable, whilst iron was apt to be uncertain. He referred to a paper by Jahvinen, in which a statement was made that tin was occluded by antimony when the antimony was precipitated by iron; he doubted this statement, and would like to have the author's views on the point.

Mr. SANVED, in reply, said that he had tested the question whether tin was occluded by antimony, and had come to the conclusion that it was not to any appreciable extent, but that iodine was the only titration solution which could be used in the presence of metallic antimony. He had not tried reducing tin by boiling with lead, but had used a lead percolate which, perhaps, was not quite the same thing; under these conditions he always had a loss of 2 per cent.

---

## The Determination of Nicotine in Tobacco.

By R. R. T. YOUNG, M.Sc.

(Read at the Meeting, October 6, 1926.)

THE first quantitative determination of nicotine in tobacco was made by Schloesing in 1846 (*Ann. Chim. Phys.*, 1847); it depended on the liberation of the nicotine by ammonia, extraction with ether, removal of the ammonia by heating, and titration of the residue with standard sulphuric acid. Inaccuracies in the method were pointed out by Skalweit (*J. Chem. Soc.*, 1882, A, 108) and by Bertrand and Javillier (*ANALYST*, 1909, 34, 219), who recommended their method of precipitation with silicotungstic acid (*ANALYST*, 1899, 24, 187) as more satisfactory. Zinnoffsky (*J. Chem. Soc.*, 1874, 497) determined the nicotine volumetrically by means of potassio-mercuric iodide, but the first method to gain general acceptance was that of Kissling (*ANALYST*, 1886, 11, 16).

Kissling's method of extraction with ether followed by steam distillation was adversely criticised by Popovici (*ANALYST*, 1890, 15, 53) and by Vedröde (*ANALYST*, 1895, 20, 255), but was defended by Kissling (*J. Chem. Soc.*, 1896, A ii, 401). Mellet's method (*ANALYST*, 1911, 36, 348) is based on the same principle.

The methods of Keller (*ANALYST*, 1898, 23, 235) and of Toth (*ANALYST*, 1902, 27, 12), like that of Schloesing, involve a simple extraction with ether, and Toth's method is recommended by Schröder (*ANALYST*, 1911, 36, 106, 411).

Spallino (*ANALYST*, 1914, 39, 43) gives the preference to the silicotungstate method provided that certain precautions are adopted, and other modifications of that method are described by Rasmussen (*ANALYST*, 1916, 41, 208), and by Shedd (*ANALYST*, 1923, 48, 610).

Other precipitation methods include that of Thoms with potassium and bismuth iodide (*J. Chem. Soc.*, 1890, A ii, 428; cf. *ANALYST*, 1905, 30, 316) and that of Guglielmelli and Hordh (*J. Chem. Soc.*, 1920, A ii, 138) with arsenotungstic acid.

The method of Tingle and Ferguson (*ANALYST*, 1917, 42, 177) depends upon the polarimetric determination of the nicotine.

Of these methods, Kissling's seems to have been the most generally used; it is often referred to as the "Official Method," and was adopted by the Association of Official Agricultural Chemists in 1904.

The following extracts from *Allen's Commercial Organic Analysis*, 1912, shows the position in that year: "Toth's method is most used in England at present, and is applicable, with slight variations, to many estimations of alkaloids. It is the most satisfactory to use. Keller's and Kissling's methods are liable to give results too high, owing to the presence of ammonia in the extracts, but have been much used on the Continent."

During the last few years the precipitation methods seem to have been more and more used, and have to a certain extent superseded the Kissling method.



From all the literature on the subject two points especially appear to merit more consideration. These are (1) To find an accurate, simple and convenient standard method for the determination of nicotine in tobacco; (2) to ascertain the error caused by the presence of ammonia liberated from the tobacco by the action of the alkali.

Kissling's method is long and troublesome; the same may be said of the silico-tungstate precipitation method of Bertrand and Javillier. The first portion of this paper consists of a critical examination of Keller's method, an attempt to justify this method, and a comparison of the results obtained by it with those obtained by the methods of Kissling and Toth.

EXPERIMENTAL.—The following tobaccos were used: "A," an average sample of New-Zealand-grown leaf from the National Tobacco Company, Napier; "B," another sample of New-Zealand-grown leaf from the National Tobacco Company; "C," a strong pipe tobacco; "D," a cheap grade cigarette tobacco; and "E," a high grade cigarette tobacco.

These were prepared by cutting them up finely and drying them for four hours in the steam-oven. After drying, the tobacco was pounded to a fine powder in a mortar, dried for a further hour, and then transferred to a well-stoppered bottle.

KELLER'S METHOD.—Keller (*loc. cit.*) recommends the use of a 10 per cent. iodeosin solution as indicator. It was found that a more dilute (1 per cent.) solution gave better results; the iodeosin was prepared from uranine, the sodium salt of fluorescein. The following indicators were also tried: litmus, methyl orange, cochineal and rosolic acid. Cochineal was found to give the best end-point, better than iodeosin; with litmus the end-point was difficult to observe, and methyl orange proved still more unsatisfactory. I consider that the indicators used might be placed in the following order: Cochineal, rosolic acid, iodeosin, litmus, methyl orange.

In this method 60 c.c. each of ether and petroleum spirit are used for extraction, and only 100 c.c. are poured off; it is evidently assumed that this volume contains  $\frac{100}{120}$  of the total nicotine in the tobacco. In order to determine whether the one extraction was sufficient to remove all the nicotine, it was followed by a second extraction with 20 c.c. each of ether and petroleum spirit, and then by a third extraction with only 10 c.c. each of the two solvents. The percentage of nicotine was first calculated on the total amount obtained from the three extractions, and then (as is done by Keller) on the amount obtained from the first extraction multiplied by  $120/x$ , where  $x$  = volume in c.c. poured off in the first extraction. The results obtained in three such experiments are given below:—

Weight of tobacco. Grms.	Duration of first extraction. Hours.	Nicotine in first extraction. Grm.	Nicotine in second extraction. Grm.	Nicotine in third extraction. Grm.	Percentage of nicotine.	
					A on three extractions.	B as per Keller.
5.956	3	0.1221	0.0240	0.0073	2.57	2.52
5.930	3	0.1183	0.0228	0.0082	2.52	2.46
6.228	3	0.1249	0.0237	0.0105	2.55	2.49

It will be seen that in each determination the result obtained by Keller's method is 0.05 per cent. or 0.06 per cent. lower than that obtained from the sum of the three extractions. It would appear from this that one extraction is hardly sufficient to extract all the nicotine, and that Keller's method tends to give low results, though the difference is very small.

It was found that there was a saving of ether by using a mixture of 10 per cent. of ether and 90 per cent. of petroleum spirit in place of the 50 per cent. of each used by Keller; with cochineal as indicator the end-point obtained was quite as sharp as when a mixture of 50 per cent. of each was used.

Keller allows the solution to stand for three hours after shaking. The results obtained for the leaf tobacco, on allowing the solution to stand 15 minutes only after shaking, were, as might have been expected, slightly lower than those obtained on allowing the solution to stand a longer time. With the other tobaccos used the results obtained on allowing the solution to stand 15 minutes only were considerably higher than when the solution stood for a longer time, and did not agree among themselves. It was noticed, also, that the end-point was rather more difficult to obtain, and it appeared as though the ethereal layer still contained a little tobacco in suspension. A possible cause of the high results therefore seemed to be that some small quantity of tobacco had not been given time to settle after shaking, and that this had absorbed some of the 20 per cent. aqueous potassium hydroxide solution originally added. In order to test this, the liquid, after standing for 15 minutes, was passed through a pleated filter paper up to the mark of a 100 c.c. flask; it was found that traces of tobacco were left behind on the filter paper. The values were then found to be in agreement with those obtained when the solution stood a longer time. The following results were obtained with tobaccos "A" and "C":—

PERCENTAGE OF NICOTINE.

Time of extraction. Hours.	"A" unfiltered.	"C" unfiltered.	"C" filtered.
24	2.53	3.42	3.34
3	2.51	3.37	—
3	2.54	3.32	—
3	2.48	—	—
1	2.45	—	—
1	2.44	—	—
0.25	2.45	3.82	3.32
0.25	—	3.70	3.25
0.25	—	3.78	—

Those experiments in which the solution was filtered ("C") are seen to give lower results than those in which the solution was not filtered, and it appears that, even after standing for 24 hours, some little tobacco must still be left in suspension. When the solutions are filtered, the results obtained by allowing the mixture to stand for 15 minutes are almost identical with those obtained after it had stood for 24 hours, so that if we filter the solution poured off, there is no advantage gained by having allowed it to stand for more than 15 minutes.

It is of interest to note that the leaf tobacco appeared to have a greater absorbing effect for the ether mixture than did the other tobaccos; it was possible to pour off the full 100 c.c. from these tobaccos, but not from the leaf. This perhaps accounts for the fact that the leaf settled more quickly after shaking, and that in this case only were satisfactory results obtained after standing for 15 minutes without filtering.

Keller recommends that "a strong current of air be passed through (the solution) to expel any ammonia present." It was thought to be of interest to test how much ammonia was removed by this means, and a U-tube, containing distilled water, acidified with one drop of dilute hydrochloric acid, and with one drop of methyl orange as indicator, was inserted between the ethereal liquid and the pump in certain of the above experiments, and a current of air passed through for two minutes. A negative result was obtained—the methyl orange did not change in colour. In other experiments a few drops of B.D.H. universal indicator were placed in distilled water in the U-tube, and on passing air through the tube for two minutes the colour of the water changed slowly from orange ( $P_H = 5.5$ ) to greenish-blue ( $P_H = 9.0$ ), showing that at least a trace of ammonia (or nicotine) had been removed. In order to find whether it was possible to determine the ammonia removed, 20 c.c. of standard 0.1 N sulphuric acid were placed in the U-tube in another experiment, and air was passed through, as above, for two minutes. On subsequently neutralising with 0.1 N sodium hydroxide solution, the average of three such experiments with different tobaccos showed a difference, attributable to ammonia, of only 0.01 c.c.

**TOTH'S METHOD.**—This method differs mainly from Keller's only in that plaster of Paris is added to the tobacco, for the purpose, it is stated, of adsorbing any ammonia present. The experiments were carried out as described (*loc. cit.*), except that 50 c.c. of the mixture were removed for titration instead of 25 c.c. It was again found necessary to filter the solution before titration.

The following results were obtained with leaf "B" and tobaccos "C" and "D"; the values for the same tobaccos by Keller's method are given for purposes of comparison.

	Leaf "B."	Tobacco "C."	Tobacco "D."
	Per cent.	Per cent.	Per cent.
Toth .. ..	3.18	3.36	2.54
	3.16	3.44	2.50
Keller .. ..	3.40	3.34	2.59
	3.39	3.32	2.63

It is seen that for tobaccos "B" and "D," Toth's method gave lower results than did Keller's, whilst for tobacco "C" the results obtained were rather higher than by Keller's method.

Rasmussen (*loc. cit.*) analysed a number of tobaccos by these methods and obtained, on the whole, lower results by that of Toth, though in one or two instances the results obtained were higher than by Keller's method.

**KISSLING'S METHOD.**—In the first two experiments on tobacco "C" by this method, a weighed quantity of the tobacco was placed in the thimble, and 10 c.c. of alcoholic sodium hydroxide solution were added from a pipette. The results obtained were very low (0.74 per cent. and 0.82 per cent.), and in the following experiments it was found necessary to mix the tobacco well with the sodium hydroxide before transferring it to the Soxhlet thimble. After extraction for five hours the extract was removed to a Kjeldahl flask, where the ether was distilled off, and, after the addition of 50 c.c. 4 per cent. sodium hydroxide solution, the residue was steam-distilled in the same flask. The results are compared with those of Keller's and Toth's methods for the same tobacco (given above):—

	Kissling. Per cent.	Toth. Per cent.	Keller. Per cent.
Tobacco "C"	3.19	3.36	3.32
	3.17	3.44	3.34
	3.21		

The percentage of nicotine is seen to be slightly lower than that obtained by either of the other two methods.

With tobaccos "B" and "D" very low results were obtained; thus two determinations with tobacco "B" gave 2.20 per cent. and 2.01 per cent. (Keller's average 3.40 per cent.), and with "D" gave 1.48 per cent. and 2.18 per cent. (Keller's average 2.61 per cent.). These two tobaccos are much bulkier than "C," and it was found that to get even ten grms. into the thimble it was necessary to compress the tobacco somewhat. It was thought that perhaps the reason for the low results obtained was that the ether in the Soxhlet could not reach all the tobacco, and consequently did not extract all the nicotine. In order to test this, a portion of the tobacco left in the thimble after extraction in one of the above experiments was removed to a second thimble and extracted for another four hours with more ether; 0.45 per cent. of nicotine was obtained from this extract after steam-distillation, showing that the first extraction had not removed all the nicotine. Two more determinations were accordingly made, in which only about seven grms. of each tobacco were taken, and loosely packed in the thimble; the results obtained, however, were still low.

From the above experiments it appears that with bulky tobaccos Kissling's method is apt to give low results, owing to incomplete extraction. The object of the method is to eliminate any ammonia which may be liberated by the action of the alkali on the tobacco.—The earlier determination by the methods of Keller and Toth, as well as the results obtained by Kissling's method for tobacco "C," indicate that the amount of ammonia present is very small. Experiments were therefore made to determine the actual amount of ammonia liberated.

**DETERMINATION OF AMMONIA.**—The first method attempted was to precipitate the nicotine as the platinichloride, to weigh this, and then ignite it and weigh the platinum residue. The theoretical amount of platinum in nicotine platinichloride is 34.1 per cent. If any ammonia is present, it will be precipitated as ammonium platinichloride, which has a smaller molecular weight than the nicotine

platinichloride, and, consequently, the percentage of platinum should be greater than 34.1.

Determinations were first made on a sample of pure nicotine (Merck.), but some difficulty was experienced in ascertaining the conditions which would lead to the theoretical 34.1 per cent. being obtained. About 0.5 gm. of nicotine was taken, and to this were added 50 c.c. of water containing 15 c.c. of *N* hydrochloric acid. A few c.c. of platinic chloride solution and about 20 c.c. of alcohol were then added, and the precipitate formed was washed on to a filter with more alcohol. After being dried for 24 hours in an evacuated desiccator and for a further two hours in the steam-oven to remove the last traces of moisture, the precipitate was weighed and finally ignited in a platinum crucible, at first gently over a small flame and then to redness, and the platinum residue was weighed. The average of three such determinations gave 32.0 per cent.

On carrying out the experiment more carefully and adding the platinic chloride drop by drop, it was noticed that two sets of crystals came down, those precipitated first being orange, those precipitated later being yellow. These were separated as completely as possible and analysed. It was found that by diminishing the amount of water used the orange crystals approximated to the compound  $B_2H_2PtCl_6$ , and when only 1 c.c. of pure hydrochloric acid was added in place of the 50 c.c. of dilute acid previously used, the result of two determinations gave the theoretical 34.1 per cent.

In each case lower results were obtained with the yellow crystals, the corresponding average being 33.5 per cent.; it is thought possible that here there is a tendency to the formation of the compound  $B_2H_2PtCl_6$ , thus accounting for the lower results.

The conditions of precipitation having been ascertained for the pure nicotine, the different tobaccos were then examined. The nicotine was extracted as in Keller's method, except that larger quantities were used. About 50 grms. of the tobacco were taken, and to this were added 30 c.c. of 20 per cent. alkali and 250 c.c. of the mixture of ether and petroleum spirit. After being shaken for twenty minutes the ethereal mixture was decanted and filtered into a separating funnel, where it was shaken for ten minutes with 10 c.c. of pure hydrochloric acid. After standing for 30 minutes the lower layer was run off and filtered. Thirty drops of the platinic chloride solution and 5 c.c. of alcohol were then added. The solution was left over-night and was finally filtered, and the filter washed with alcohol. Yellow crystals were precipitated from the filtrate on addition of more platinic chloride, and both sets of crystals were dried as above and analysed separately.

The following results were obtained with the different tobaccos:—

		PERCENTAGE OF NICOTINE.	
		Orange crystals.	Yellow crystals.
Pure nicotine	.. ..	34.1	33.5
Leaf "B"	.. ..	33.8	33.2
		33.6	33.3
Tobacco "C"	.. ..	34.2	32.8
Tobacco "D"	.. ..	33.9	33.6

As in the case of pure nicotine, low results were also obtained with the other tobaccos when 50 c.c. of dilute acid were used in place of the smaller volume of concentrated acid. Thus the percentages of platinum obtained in two experiments with tobacco "C" were 32.9 and 33.0. The orange and yellow crystals were here not separated, and it will be seen that the results are considerably lower than those for the orange crystals obtained when concentrated acid was used. (See table above.)

Whilst the results obtained by this platinichloride method appear to be inconclusive as to the actual amount of ammonia present, the inference is that either there is no ammonia or else the amount present is extremely small.

Auric chloride was also tried in place of platinic chloride with pure nicotine, but did not prove satisfactory. Nicotine aurichloride appears to be more soluble than the platinichloride, and only a small precipitate was obtained; this, on analysis, gave 46.1 per cent., as against the theoretical 46.8 per cent.

PRECIPITATION OF NICOTINE WITH IODINE.—Another method attempted for the determination of the ammonia was by precipitation of the nicotine with iodine, followed by distillation of the ammonia. Harrison and Self (ANALYST, 1912; 37, 311) had previously used this method for the separation of the nicotine from ammonia. It was found to lead to more definite results than the platinichloride determinations.

The amount of iodine necessary to precipitate all the nicotine was first ascertained. A standard iodine solution was prepared by dissolving 50 grms. of pure resublimed iodine and 100 grms. of potassium iodide in distilled water and making up the solution to a litre. In six determinations, six different volumes of iodine solution (multiples of 25 c.c.) were added to the same small quantity of nicotine in each case, 50 c.c. of water containing 15 c.c. of *N* hydrochloric acid having previously been added to the nicotine. After standing for 24 hours the solutions were filtered and the precipitates well washed with potassium iodide. Excess iodine in each filtrate was then removed by means of sodium thiosulphate crystals, and the solution made alkaline and finally distilled into 25 c.c. of 0.1 *N* acid. It was found that 150 c.c. of the iodine solution were required to precipitate completely all the nicotine (weight, 0.38 gm.). In the following table are given the number of c.c. of 0.1 *N* acid which combined with the unprecipitated nicotine on the addition of different volumes of iodine solution:—

Volume of iodine solution, c.c.	25	50	75	100	125	150
Volume of 0.1 <i>N</i> acid neutralised, c.c.	20.30	11.20	1.92	1.12	0.38	0.00

The weight of iodine in 150 c.c. of this solution is 7.50 grms., and it is seen that to completely precipitate the nicotine twenty times its weight of iodine is therefore required. Harrison and Self (*loc. cit.*) added only ten times the weight of iodine to precipitate the nicotine, and, whilst their results are not given in the ANALYST abstract, it is inferred that they obtained an appreciable amount of ammonia in the tobaccos they examined; this is doubtless due to their having estimated some of the nicotine as ammonia owing to incomplete precipitation.

This method can be used to ascertain the formula of the insoluble nicotine iodide by measuring the amount of iodine unprecipitated. The solution, after filtration, was accordingly titrated with 0.1 *N* sodium thiosulphate solution. The results agreed approximately with the formula  $B, XKI, 7I_2$ .

Experiments were now carried out to determine whether, under the same conditions, any ammonia was precipitated. It was found that on adding excess of iodine and 50 c.c. of dilute hydrochloric acid to 10 c.c. of a standardised 0.05 *N* ammonia solution and allowing the mixture to stand for 24 hours, the whole of the ammonia present was obtained on subsequent distillation. Further experiments carried out with nicotine and ammonia together showed that the whole of the ammonia could be recovered after treatment with iodine and distillation, but that now a larger excess of iodine was required for the complete precipitation of the nicotine. It would appear that ammonia has some solvent action on the nicotine iodide.

AMOUNT OF AMMONIA IN TOBACCO.—In order to determine the amount of ammonia, if any, in the different tobaccos, the nicotine was extracted in a manner similar to that in the platinichloride determinations. After the ethereal mixture had been shaken for ten minutes with 50 c.c. of water containing 15 c.c. of *N* hydrochloric acid and left for 15 minutes, the lower acid layer was run off, and the amount of iodine required to precipitate the nicotine was added. After standing for 24 hours the solution was filtered, excess of thiosulphate added, and then sodium hydroxide until alkaline. The ammonia was determined, as before, by distillation into standard acid. Leaf "B" and tobaccos "C," "D," and "E" were all examined in this manner, and in no case was more than 0.35 c.c. of the 0.1 *N* acid found to be neutralised. The following results were obtained showing the percentage error in Keller's nicotine determination due to the presence of ammonia:—Leaf "B," 0.04; Tobacco "C," 0.03; Tobacco "D," 0.01; and Tobacco "E," 0.04.

Since the equivalent weight of ammonia is only about one-fifth of that of nicotine, the actual percentage of ammonia present is very small indeed.

Finally, the ammonia determination was carried out actually in conjunction with Keller's method. After neutralisation of the base, the liquid was shaken with 50 c.c. of dilute acid as before; the lower layer separated after standing, and the nicotine was precipitated with excess of iodine. On distillation with alkali the amounts of acid neutralised in the case of tobaccos "D" and "E" corresponded to 0.03 and 0.04 per cent. of nicotine, respectively.

The literature on the subject of nicotine determinations in tobacco contains many statements regarding the presence of ammonia, and numerous devices have been suggested to eliminate the error thus caused, although, strangely enough, no one appears to have made an effort actually to determine the amount of ammonia present. We have seen that Keller (*loc. cit.*) passes a current of air through the extract to expel the ammonia, whilst Toth (*loc. cit.*) adds plaster of Paris to adsorb the ammonia, and Kissling (*loc. cit.*) distils with steam to separate the nicotine from ammonia.

All the precipitation methods (*e.g.* those of Harrison and Self, and of Bertrand and Javillier) are devised to separate the nicotine from ammonia. V. Vedröde (*loc. cit.*) states that Kissling's method is liable to give high results unless care is taken to get rid of the ammonia completely before exhausting with ether, though he later attributed the high results to sodium hydroxide carried over in the steam distillation.

Rasmussen (*loc. cit.*) outlines an elaborate precipitation method for the determination of the nicotine in order that the presence of ammonia will not interfere with the results. In Allen's *Commercial Organic Analysis* is found the statement (quoted earlier) that "Keller and Kissling's methods are liable to give results too high, owing to the presence of ammonia."

MODIFICATION OF KELLER'S METHOD.—The results of the present work seem to prove definitely that the amount of ammonia present in tobaccos is very small indeed, and that the error caused by its presence is almost within the experimental error. This being the case, it is suggested that the following modification of Keller's method furnishes both an accurate and simple method for the determination of the nicotine content: Six grms. of the dried and powdered tobacco are treated in a stoppered bottle with 100 c.c. of petroleum spirit, 20 c.c. of ether, and 10 c.c. of 20 per cent. aqueous potassium hydroxide solution. The mixture is well shaken for 15 minutes, and, after standing for a similar interval, 100 c.c. of the ethereal liquid are filtered off. Ten c.c. of alcohol, 10 c.c. of water, and a few drops of a dilute cochineal solution are added, and the whole is well shaken, causing the cochineal and the nicotine to pass into the aqueous liquid. A slight excess of 0.1 *N* hydrochloric acid is now added, the liquid again shaken, and the excess acid titrated with 0.1 *N* sodium hydroxide solution. One c.c. of acid = 0.0162 gm. of nicotine.

If the presence of ammonia is suspected and it is desired to make a correction for it, the following procedure may be adopted: The above solution is run into a separating funnel, the last traces being washed in with 50 c.c. of water containing 15 c.c. *N* hydrochloric acid. After being shaken for ten minutes the liquid is allowed to stand for 15 minutes, when the lower aqueous layer is run off. To this are added 150 c.c. of an iodine solution containing 50 grms. of iodine and 100 grms. of potassium iodide per litre. After standing overnight the solution is filtered and the filter paper well washed with potassium iodide solution. Crystals of sodium thiosulphate are added till the liquid becomes colourless, when it is distilled with sodium hydroxide into 25 c.c. 0.1 *N* acid. The distillation is continued for nearly an hour, and the acid then titrated with 0.1 *N* alkali solution.

#### APPENDIX.

A. THE FRACTIONAL EXTRACTION OF NICOTINE FROM TOBACCO.—Graham and Carr (*ANALYST*, 1924, 49, 247) determine the nicotine in various tobaccos by Kissling's method, and also extract the nicotine from the same tobaccos by using several solvents in succession and without the initial addition of



caustic soda. In many cases they obtain more nicotine by the extraction with different solvents than is actually present in the tobaccos as determined by Kissling's official method. A few of their results are as follows:—

Tobacco.	Nicotine extracted by		Total nicotine. Per cent.	Total nicotine by official method. Per cent.
	(1) ether. Per cent.	(2) alcohol. Per cent.		
a.	0.17	1.05	1.22	3.83
b.	0.33	3.54	3.87	2.56
c.	3.17	1.65	4.82	4.59
d.	2.43	1.52	3.95	2.66

Whilst they do not appear to have drawn any definite conclusions from their results, it seems that here, again, Kissling's method proved untrustworthy.

Similar experiments to theirs were made with leaf "B" and tobacco "C," the ether used being distilled over sodium, and the alcohol distilled over quicklime. The extraction with each solvent was carried out in a Soxhlet apparatus for 15 hours. It will be seen that with both tobaccos the amount of nicotine obtained from the different solvents was less than the total nicotine, as determined by Keller's method.

Tobacco.	Nicotine extracted by		Total nicotine. Per cent.	Total nicotine by Keller's method. Per cent.
	(1) ether. Per cent.	(2) alcohol. Per cent.		
Leaf "B"	0.73	2.18	2.91	3.40
Tobacco "C"	0.14	2.90	3.04	3.33

B. THE COMPOSITION AND QUALITY OF TOBACCOS.—It is generally agreed that only considerable differences in the amount of the various constituents of tobacco can give any conclusive indication of its quality. The strength appears to be dependent less on the amount of nicotine than on the percentage of protein. Excess of protein causes poor combustibility, and hence tends to make the tobacco rank.

The total nitrogen in the different tobaccos was determined by Kjeldahl's method, and by subtracting from this the nitrogen as nicotine, the nitrogen as protein is obtained; multiplication of this by the protein factor (6.25) gives the percentage of protein. The results are as follows:—

Tobacco.	Nitrogen			Nicotine. Per cent.	Nitrogen as Nicotine. Per cent.	Nitrogen as Protein. Per cent.	Protein. Per cent.
	(1) Per cent.	(2) Per cent.	Average. Per cent.				
Leaf "B"	2.13	2.16	2.15	3.40	0.59	1.56	9.75
Tobacco "C"	2.39	2.37	2.38	3.33	0.57	1.81	11.31
"   "D"	1.80	1.82	1.81	2.60	0.45	1.36	8.50
"   "E"	1.73	1.70	1.72	2.43	0.42	1.30	8.13

It will be seen that the strong pipe tobacco "C" contains a little more nicotine than the milder cigarette tobaccos "D" and "E," while its protein content is

considerably greater. Again, the cigarette tobacco "D," of poorer quality, contains very little more protein than the high class tobacco "E." An analysis made in this laboratory on another sample of "E" a year previously showed, however, a much lower protein content.

C. THE DETERMINATION OF NICOTINE IN INSECTICIDES.—Experiments were made to ascertain whether the percentage of nicotine in insecticides could be determined satisfactorily by Keller's method, or whether the presence of ammonia interfered with the results.

Two different liquid insecticides were used, and in both cases the percentage of nicotine was determined in the usual manner by the modified Keller's method, it being found convenient here to use a separating funnel in place of the stoppered bottle previously employed. The solutions were then treated with sufficient iodine to precipitate all the nicotine and distilled with sodium hydroxide, as before described.

In the case of the first insecticide used, two determinations of the nicotine gave 17.70 and 17.12 per cent. On precipitating with iodine and distilling with sodium hydroxide into 25 c.c. of 0.1 *N* acid, not more than 0.2 c.c. of acid was neutralised in either case, thus disclosing an error of not more than 0.1 per cent. of nicotine in the above results.

The determinations of nicotine in the second insecticide (marked 40 per cent.) gave 46.85 and 46.50 per cent. Here, again, not more than 0.2 c.c. of 0.1 *N* acid combined with any ammonia given off, making the corrected results approximately 46.80 and 46.45 per cent., respectively (this strong insecticide is well diluted before use as a spray).

It appears, therefore, that the percentage of ammonia does not appreciably affect the results obtained in the determination of the percentage of nicotine in insecticides by the modified Keller's method.

I wish to thank Professor P. W. Robertson, Victoria University College, New Zealand, for much helpful advice in connection with this paper.

#### DISCUSSION.

Mr. CHASTON CHAPMAN said that he had made a few experiments with the object of comparing Mr. Young's method with the one which he usually considered the most accurate, namely, the silicotungstate process. The result, as might be seen from his results, was very satisfactory indeed, the two methods agreeing almost exactly.

Young's Method, per cent.	..	..	1.79	2.09	3.06	2.23	2.09
Silicotungstate Method, per cent.	..	..	1.77	2.06	2.92	2.30	2.05

It should perhaps be added that the tobaccos he had tried had all been cigarette tobaccos of more or less the same general character. Whether the agreement would have been as good in the case of tobaccos differing very widely from these he was unable, of course, to say.

## The Rapid Determination of Opium in Stomach Contents.

By E. ROADLEY DOVEY, A.R.C.Sc., F.I.C.

*(Read at the Meeting, December 1, 1926.)*

THIS laboratory, in common with many other laboratories in the East, is called upon to deal with a large number of cases of opium poisoning. The majority of these are suicidal, and the patient is admitted to hospital with a history of having taken opium and displaying the usual symptoms. The stomach is at once washed out, and to confirm the diagnosis the stomach washings are sent in for examination.

The filtered contents are usually dark reddish brown in colour, frequently smelling of opium, and, as a rule, give strong reactions for alkaloids and meconic acid.

It is very desirable to be able to ascertain rapidly the quantity of opium present in the liquid, and the following method has been found useful and rapid.

A standard solution of opium is prepared from the ordinary prepared opium made for smoking, and this has itself been standardised to contain 10 per cent. of morphine and 5 per cent. of meconic acid. One gm. of such opium is weighed out and made up to 250 c.c. One c.c. of this solution is then equivalent to 0.004 gm. of opium, or 0.0615 grain.

From 1.0 to 10 c.c. of the filtrate from the stomach washings or stomach contents, which have given positive reactions for meconic acid, alkaloids and morphine, are taken, the volume taken depending on the strength of the reactions obtained. This is pipetted into a 50 c.c. Nessler cylinder, into which are then introduced about 25 c.c. of water, two drops of 1:3 hydrochloric acid, 5 c.c. of saturated mercuric chloride solution, and 5 drops of ferric chloride solution, and the whole is made up to the 50 c.c. mark, with stirring.

This mixture is now compared with a standard prepared as follows:— To 25 c.c. of water in another similar cylinder are added, as above, two drops of 1:3 hydrochloric acid, 5 c.c. of saturated mercuric chloride solution, and 5 drops of ferric chloride solution. The standard solution of opium is then added from a burette, with stirring, until the colours in the two cylinders are nearly matched, after which water is added to the standard until the volume is nearly the same as the other, and the final adjustment is then made. It is possible to obtain results accurate to 0.5 c.c. of the above solution, and in the majority of cases here from 15 c.c. to 25 c.c. are required.

The addition of the dilute hydrochloric acid and mercuric chloride solution inhibits colorations due to acetates and thiocyanates in normal quantities. The colour produced by adding ferric chloride solution to 2 c.c. glacial acetic acid in 50 c.c. of water is discharged by the addition of two drops of 1:3 hydrochloric acid.

Thiocyanates may exist in the gastric juice in quantities equivalent to 0.01 per cent. of thiocyanic acid, but the colour produced by the addition of ferric

chloride solution to much less dilute solutions of thiocyanates, is discharged on the addition of 5 c.c. of saturated mercuric chloride solution.

In Hongkong the only opium that is easily obtainable is that prepared by the local opium monopoly, and this is a more or less standardised product. By employing this for preparing the standard solution and using the above process it is possible to obtain a figure for the amount of opium present in terms of the kind of opium most likely to have been taken.

It is probable that the same colorimetric process could be utilised for the determination of opium in many other liquids, since all data regarding opium (fatal doses, etc.) can only refer to average or standard opium, such, for example, as that which has been standardised to contain 10 per cent. of morphine and 5 per cent. of meconic acid.

GOVERNMENT LABORATORY,  
HONGKONG.

---

## 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.*

---

### ALLEGED USE OF MARKING INK IN ANCIENT EGYPT.

ON page 137 of Budge's book *The Mummy* (2nd ed., 1925) occurs the following interesting passage: "It is worthy of note that Egyptian ladies marked their linen with indelible ink; see the winding sheet of Tchehuti-Sat (B.M. 37105)."

The fabric here mentioned is a long rolled-up linen sheet with a fringe at the end, and the name, in a brown pigment, runs horizontally across the material just above the fringe. As no reasons are given for the conclusion that indelible ink was used for the purpose, I applied a series of micro-chemical tests to the pigment, and I am indebted to the kindness of Dr. Alexander Scott, Director of the Research Laboratory of the British Museum, for the opportunity of making this examination of one or two of the fibres of the fabric.

The brown pigment was readily and completely bleached by hypochlorite, leaving no residual particles of carbon; hence it was not a faded carbon ink of the type described by Lucas (*ANALYST*, 1922, 47, 11). Other tests showed that neither iron nor copper was present. It seems probable, therefore, that this pigment was an organic colouring matter (possibly bistre free from carbon), and that it was attached to the material in the form of a paint—a principle used in stencilling modern fabrics.

It is only in the sense that writing which has come down to us through the ages is relatively permanent that this pigment can be described as "indelible," and it has nothing in common with the indelible marking inks of to-day, the pigment of which is formed within the fibres of the material after the application of the ink.

C. AINSWORTH MITCHELL.

## 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.*

### COUNTY OF LANCASTER.

#### ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1925.

THE total number of samples examined under the Food and Drugs Acts during the year was 4589, of which 487 were adulterated or not up to standard.

**MILK.**—Of the 2990 samples examined, 383 were adulterated, deficient, or dirty. Eighteen samples were artificially coloured with annatto, and 3 (all from one source) contained 10 to 25 parts of formaldehyde per million. A slight improvement in cleanliness was noted. Five samples contained from 5 to 8 parts of cow-dung per 100,000, and 3 contained 11, 12 and 13 parts respectively.

**CREAM CHEESE.**—Two samples, sold as "cream cheese" by the same vendor, were labelled "Bondon," and in small letters "Curd Cheese." Both had been prepared from milk which had been deprived of nearly the whole of its fat.

**JAM.**—Four samples (3 informal) made by one firm contained apple pulp, the amount in the formal sample being 5 per cent. All the samples were labelled "Fruit juice added to give consistency," but such a declaration does not convey to the purchaser the fact that the jam contained apple pulp.

**SAUSAGES.**—Three samples contained high percentages (56 to 60) of water, but there is no legal limit, and these samples were on the border line of decided cases.

**LOBSTER PASTE.**—Nine samples of lobster paste and one of crab and lobster paste consisted mainly of fish paste. Only two out of nine brands examined contained a material quantity of lobster.

**LEAD IN TINNED CORNED BEEF.**—An informal sample was found to contain lead, and this was followed up by two formal and two informal samples of the same brand from the same shop.

All contained traces of lead, but much less than in the first test. The lead was generally unequally distributed in the samples. Thus the original informal sample contained 1-7th grain per pound in the first portion examined, but another portion of the same sample was almost free from lead. The first formal sample contained 1-15th grain per pound in one portion and only a minute trace in another.

Quantities of lead of the order of 1-7th grain per pound are very objectionable in tinned meat, but this amount was evidently localised, and may have been due, at least in part, to minute particles of solder. The average lead content of the four subsequent samples varied from 1-30th to 1-50th grain per pound. It is very desirable that foodstuffs put up in soldered tins should be protected from contact with the solder.

**ICE CREAM.**—Six samples were submitted in connection with an outbreak of sickness, but no injurious ingredient was found. Incidentally it was found that three were prepared from skimmed milk and three from ordinary milk. There is no standard for "ice cream" in this country, but such a description is a misnomer as applied to such samples as the above.

**INVALID WINE.**—This sample was labelled "Liebig's Invalid Wine. Health. Strength. Vigour. Strengthening and Nutritious. Recommended by the Medical Profession. Take a wineglassful three times a day. Non-excisable." This label conveys misleading and exaggerated impressions of the nature and value of the article, the useful medicinal properties of which depended solely on the presence of 15 minims of diluted phosphoric acid B.P. per fluid ounce. For the rest, it was a non-alcoholic coloured and flavoured sugar solution, containing half a grain of quinine and  $3\frac{1}{2}$  grains of salicylic acid per pint, with a possible trace of meat extract, not exceeding 0.5 per cent. The sample was an informal one, and the manufacturer was cautioned by the Local Authority concerned.

It is high time that regulations for the sale of medicated wines and patent medicines generally were imposed on the lines indicated in the Report of the Committee on this subject issued about twelve years ago.

**SPIRITS.**—Ten samples of whiskey and one of gin were diluted below the present legal limit of 35 degrees under proof. In one case a notice was exhibited in the bar as follows: "To meet the requirements of the Food and Drugs Acts. Notice is hereby given that all spirits sold at this establishment are diluted, and that no alcoholic strength will be guaranteed." The sample in question was 42.6 degrees under proof.

W. COLLINGWOOD WILLIAMS.

## 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.*

### TABLE VINEGAR.

ON November 5 a tradesman was summoned at Birmingham for selling vinegar not of the nature, substance and quality demanded.

Mr. Digby-Seymour, for the prosecution, said that an agent of the inspector had asked for malt vinegar, but that the defendant had replied that she had not malt vinegar, but could supply table vinegar. The purchaser had then bought a pint of table vinegar for 3d., which, when analysed, was found to be artificial vinegar, and not table vinegar. The prosecution suggested that by "table vinegar" was implied a vinegar of rather superior quality, in the same way as "table salt" conveyed the idea of a superior salt. He believed that years ago vinegar was put into bottles and labelled "table vinegar," and that the price charged was higher than for ordinary vinegar, or for malt vinegar even.

Mr. J. F. Liverseege, F.I.C., City Analyst, said that three descriptions of vinegar had been used. First, there was artificial vinegar, which was acetic acid diluted and coloured with burnt sugar. The sample in question was artificial vinegar. Malt vinegar was manufactured from malt and grain by alcoholic fermentation, followed by a process of acetification. Vinegar was similarly prepared by fermentation and acetification, but more or less of the malt and grain was replaced by sugary matter. Artificial vinegar was made by a cheaper process. The word "table" suggested to him something superior for use on the table, and not something inferior. Inferior vinegar would be used for pickling. Artificial vinegars had much the same smell as fermentation vinegars, but had a harsher taste.

Mr. Liverseege added that in the nine years ending last year he had analysed 786 samples of vinegar bought by Birmingham inspectors, and only six of them were artificial vinegars. From his own knowledge he could say that in 1893 several offenders were convicted for selling artificial vinegar as vinegar, and that an appeal to the Birmingham Quarter Sessions had been dismissed with costs (*cf.* ANALYST, 1893, 18, 208). Ever since then he had taken up the position that artificial vinegar could not be regarded as vinegar.

The Chairman of the Bench said that they considered the case proved, but, as there was no intention to defraud, only a nominal fine of 5s. would be imposed.

---

### FLOUR CONTAINING ACID CALCIUM PHOSPHATE.

THE manager of a co-operative society was summoned at Omagh for having sold flour containing 2.75 per cent. of acid calcium phosphate.

The solicitor for the defence said that the phosphate was generally used by millers to improve the quality of flour, and that there was no evidence that this flour contained any deleterious matter or that it was sold to the prejudice of the public.

A member of a firm of flour importers gave evidence that it was the practice of millers to put acid calcium phosphate into flour to improve it and to make it more readily baked. He had never heard of a prosecution of this kind before.

The Chairman of the Bench said that the magistrates were unanimous in dismissing the case, as they did not believe that 2.75 per cent. of the added substance was deleterious.

---

### PRUSSIC ACID IN LINSEED MEAL.

ROBINSON *v.* STURDY.

ON November 10 an appeal was heard in the King's Bench Division of the Northern High Court, Belfast, from a decision of the County Court Recorder, who had awarded £20 damages with costs to a farmer, for the loss of two calves which had died from the effects of prussic acid, alleged to have been contained in linseed meal sold by the defendant as cattle food.

Dr. J. Hawthorne, Public Analyst for County Down, gave evidence that he had analysed the meal, and had found that it was capable of generating 1.06 per cent. of prussic acid.

The Judge, giving his judgment on November 12, said that, although this linseed meal did contain this high proportion of prussic acid, yet he had come to the conclusion that, if properly prepared, it would be suitable for cattle food, and that the death of the calves was due to the negligence or carelessness with which it was prepared by the plaintiff. He could not hold the defendant responsible, because there was no regulation as to the amount of prussic acid which might be in the meal. The defendant was one out of hundreds of traders in the country towns who were selling this meal without having anything to do with its manufacture. He must reverse the decision of the Recorder. He was sorry for the loss of the plaintiff, but he had to decide the case apart from any feelings of sympathy.

## Queensland.

### REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDING JUNE 30TH, 1926.

THE Government Analyst, Mr. J. B. Henderson, F.I.C., reports that 7015 samples were examined during the year, of which 1892 were for the Customs, 2011 for the Health Department, and 102 for the Police.

**MILK.**—Of the 1027 formal samples of milk, 792 were satisfactory. Analysis of the figures for the last five years shows that, on an average, in Queensland about one person in every eight is supplied with adulterated milk. The reductase test showed that many samples were still unsatisfactory as regards bacterial contamination.

**PRICKLY-PEAR HONEY.**—A sample of honey made by bees from the flowers of the prickly-pear was examined. It was of a very pale straw colour and had an agreeable, but not distinctive, flavour. Its composition was as follows:—Water, 20·00; cane sugar, 0·95; invert sugar, 77·70; dextrin, 0·23; mineral constituents, 0·11; acidity (as formic acid), 0·14; tannin substances, nil; and undetermined, 0·87 per cent.

**ESSENCE OF VANILLA.**—In view of representations by manufacturers that the alcoholic strength prescribed as the standard for vanilla essence (50 per cent. by weight) should be lowered to 40 per cent., a series of experiments was made with alcohol of different strengths (30 to 65 per cent.). The results (given in tabular form) showed that most of the alcohol-soluble material was extracted from the bean in 24 hours, but that the aroma of the essence was improved by longer contact. The lead values obtained fell within the normal limits (0·4 to 0·75), and the vanilla content was not less than 0·1 per cent. The essences prepared with 30 and 35 per cent. alcohol were colloidal, and very little of the reddish-brown resin was dissolved. The conclusion drawn is that 40 per cent. alcohol is a fairly good solvent, but that better results are obtained with alcohol of 45 to 55 per cent. strength, and that there is no justification for altering the standard.

**LEMON CHEESE.**—According to the Queensland regulations lemon cheese consists of a mixture of butter, eggs, sugar and lemon-flavouring substances, and must be free from foreign fat, starch, glucose, gelatin, preservatives and artificial colour.

Analyses of the products of eleven manufacturers making lemon cheese in Queensland gave the following results:—

	A	B	C	D	E	G
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Sugars ..	68·0	62·0	66·0	65·0	60·0	61·0
Butter ..	3·0	10·0	4·5	5·4	2·7	2·5
Citric acid ..	0·9	0·6	0·8	0·9	1·1	1·0
Egg ..	16·0	9·0	6·0*	17·0	22·0	23·0
Water ..	12·1	18·4	22·7	11·7	14·2	12·5
	100·0	100·0	100·0	100·0	100·0	100·0
	Conformed to standard	Artificially coloured	Contained glucose, starch, and added colour	Contained glucose	Conformed to standard	Conformed to standard



	H	I	J	K	L
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Sugars .. .. .	63.0	65.0	58.0	65.0	60.0
Butter .. .. .	11.0	14.0	9.1	1.0	4.0
Citric acid .. .. .	0.8	0.8	0.3	0.3	0.5
Egg .. .. .	7.4	1.5	17.0	2.0*	18.0
Water .. .. .	17.8	18.7	15.6	31.7	17.5
	100.0	100.0	100.0	100.0	100.0
	Artificially coloured	Contained glucose, preservative, and added colour	Contained glucose and added colour	Contained glucose, starch, and added colour	Contained glucose

\* Includes starch.

STABILITY OF CALCIUM CYANIDE.—Quantities of 0.5 gram. of powdered calcium cyanide and of sodium cyanide were exposed to the air for different periods, with the following results:—

Air Temperature—Average 22° C.					
	Initial amount.	After 30 mins.	After 45 mins.	After 75 mins.	After 2 hrs.
Calcium cyanide, per cent. ..	40.5	34.0	26.0	15.0	7.0
Sodium cyanide, per cent. ..	75	—	—	—	—
	After 24 hrs.	After 2 days	After 4 days	After 5 days	After 10 days
Calcium cyanide, per cent. ..	4.0	2.0	2.0	1.3	—
Sodium cyanide, per cent. ..	74	—	—	65	60

After five days the calcium cyanide increased about 10 per cent. in weight, but it did not become deliquescent like the sodium cyanide, which in the same time absorbed its own weight in water.

Calcium cyanide and sodium cyanide in 1 per cent. aqueous solution were also exposed to the air at an average temperature of 22° C. The solutions, when tested at intervals for twenty-two days, were found to decompose at approximately the same rate, the calcium cyanide being only slightly faster in its decomposition rate.

The investigations showed that calcium cyanide is by no means a safe substance to handle, and that several of the claims made for it as a harmless substance were misleading.

## Siam.

### THIRD REPORT OF THE GOVERNMENT LABORATORY.

THE Director of the Government Laboratory of Siam, Mr. A. Marcan, F.I.C., gives an account of the work done in the two years ending March 31, 1926. During this period 692 analyses were made for different Departments, and various investigations were carried out.

CHEMICO-LEGAL WORK.—Of the 41 articles examined, 17 were found to contain poisonous substances, *viz.*, arsenic in 2, atropine in 8, atropine and mercury in 1, ethyl alcohol in 1, a poisonous glucoside in 1, mercuric oxide in 1, strychnine in 2, and a glucoside (ascribed to oleander, *Nerium odorum*) in 1.

**OLEANDER POISONING.**—The case (of attempted suicide) ascribed to *Nerium odorum* (Oleander, Yi tō) is the first of the kind recorded. The symptoms were slight contraction of the pupils, abdominal pains, severe convulsions and cramps, and frothing at the mouth. Glucosides isolated from the roots of *Nerium odorum* gave colour reactions similar to those observed in this case. It is possible that the glucosides of this shrub are similar in effect to those of the fruit of yellow oleander, Yi tō luang (*Thevetia nerifolia*).

**DECIPHERING OF CHARRED DOCUMENT.**—A problem of deciphering printed characters on charred paper was submitted, and was effected by chemical means.

**ANALYTICAL VALUES OF HYDNOCARPUS OIL AND ITS ETHYL ESTERS.**—The following data have been obtained in the course of 3½ years in the examination of oil of *Hydnocarpus anthelmintica* oil, and the ethyl esters prepared from it for the treatment of leprosy:—

	Sp. gr. 30 <sup>o</sup> /4 <sup>o</sup> C.	M.pt. ° C.	Acid value as oleic acid. Per Cent.	Sapon. value.
Oil .. .. .	0.943-0.950	20.2-23.4	0.2-9.8	191.4-226.5
Esters .. .. .	0.891-0.903	—	0.04-1.3	180.9-200.6
		Iodine value, Wijs.	[α] <sub>D</sub> <sup>30</sup> .	n <sub>D</sub> <sup>30</sup> .
Oil .. .. .		88.6-99.6	49.5-51.5	1.4733-1.4753
Esters .. .. .		71.3-83.6	35.9-47.4	1.4534-1.4590

The esters are blended so that the acid value does not exceed 0.7 per cent. as oleic acid; it is usually considerably lower.

**CHEMISTRY OF OPIUM SMOKING.**—It was proved that opium smoke contains only traces of alkaloids. The smoke from 5 grms. yielded only 5 mgrms. of crude morphine and 5 mgrms. of other alkaloids. This would correspond to only 0.0025 gm. of crude alkaloids in the smoke from the 1.25 grms. of opium normally smoked. It would appear that the physiological effects of opium smoking must be largely due to volatile decomposition products in the prepared opium, and that the popular conception that opium smoking and morphine addiction are synonymous is incorrect. In the preparation in the factory the opium is roasted, and the smoker himself heats it over a naked flame, whereby the loss (excluding moisture) was found to be 12.7 per cent. of the prepared opium.

## Ministry of Health.

### STATUTORY RULES AND ORDERS, 1926, No. 1557.

#### PUBLIC HEALTH, ENGLAND.

##### THE PUBLIC HEALTH (PRESERVATIVES, &c., IN FOOD) AMENDMENT REGULATIONS, 1926. DATED DECEMBER 10, 1926, MADE BY THE MINISTER OF HEALTH.

71203.\*

The Minister of Health, in the exercise of the powers conferred upon him by the Public Health Act, 1875, the Public Health (London) Act, 1891, the Public Health Act, 1896, the Public Health (Regulations as to Food) Act, 1907, and the Butter and Margarine Act, 1907, and of every other power enabling him in that behalf, hereby makes the following Regulations, with the consent of the Commissioners of Customs and Excise, so far as they apply to the Officers of Customs and Excise, that is to say:—

1. These Regulations may be cited as the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1926.

\* H.M. Stationery Office. Price 1d. net.

2. The Public Health (Preservatives, &c., in Food) Regulations, 1925, shall be amended as follows:—

- (1) For the proviso to Article 1 there shall be substituted the following proviso,—  
“Provided that—
- (i) the Regulations shall come into operation on the 1st day of July, 1927, so far as they relate to bacon, ham and egg yolk, and on the 1st day of January, 1928, so far as they relate to butter and cream and to the revocation of such of the provisions of the Public Health (Milk and Cream) Regulations, 1912, and the Public Health (Milk and Cream) Regulations, 1912, Amendment Order, 1917, as relate to cream; and
  - (ii) so far as the Regulations prohibit the sale of an article of food containing any preservative which is necessarily introduced by the use in its preparation of preserved margarine, preserved egg yolk, preserved bacon, preserved ham, preserved cream, or preserved butter, they shall come into operation on the following dates, viz.—  
(a) the 1st day of July, 1927, where the preservative has been so introduced by the use of preserved margarine; (b) the 1st day of January, 1928, where the preservative has been so introduced by the use of preserved bacon, preserved ham, preserved egg yolk or preserved cream; and (c) the 1st day of July, 1928, where the preservative has been so introduced by the use of preserved butter.”
- (2) In the definition of “preservative” contained in Article 2 (1) the word “glycerine” shall be inserted after the word “vinegar.”
- (3) For Article 4 (2) there shall be substituted the following paragraph:—“(2) The following provisions shall have effect with respect to any of the articles of food mentioned in paragraph 1 of the Second Schedule to these Regulations which contains any preservative specified in Part I of the First Schedule as permissible in the case of such article, that is to say—
- (a) A person who exposes or offers any such article for sale by retail shall at the time when it is so exposed or offered either cause the article to be labelled in accordance with the Rules set out in the said Second Schedule, or cause a notice to the effect that the article contains preservative to be exhibited in a conspicuous place so as to be easily readable by a customer; and
  - (b) A person who sells any such article shall cause it to be labelled in accordance with the said Rules at the time when it is delivered to any purchaser, agent or broker:
- Provided that,—
- (i) neither the requirement mentioned in paragraph (a) nor that mentioned in paragraph (b) shall apply where the article is exposed or offered for sale by retail or delivered to a customer in a hotel, restaurant or other such place for consumption on the premises; and
  - (ii) the requirement mentioned in paragraph (b) shall not apply where the article is sold by retail and delivered to the purchaser at the vendor's premises or stall if such a notice as is mentioned in paragraph (a) is there exhibited as provided in that paragraph.”
- (4) The words “in the case of butter” shall be omitted from Article 12.
- (5) In Part I of the First Schedule for the items numbered 2, 6 and 7 there shall be substituted the following items,—

Food.	Preservative.	Parts per Million.
2. Fruit and fruit pulp (not dried) for conversion into jam or crystallised glacé or cured fruit as defined in items 6 and 7:		
(a) Cherries .. .. .	Sulphur Dioxide	3,000
(b) Strawberries and Raspberries .. .. .	Do.	2,000
(c) Other fruit .. .. .	Do.	1,500
6. Jam (including marmalade and fruit jelly prepared in the way in which jam is prepared) .. .. .	Sulphur Dioxide	40
7. Crystallised glacé or cured fruit (including candied peel) .. .. .	Do.	100
7a. Fruit and fruit pulp not otherwise specified in this Schedule .. .. .	Do.	350

(6) In paragraph 5 of the Second Schedule the words "on and after the 1st day of July, 1927," shall be inserted after the word "shall" in the fifth line of that paragraph.

3. Copies of the Public Health (Preservatives, &c., in Food) Regulations, 1925, printed under the authority of His Majesty's Stationery Office, may be printed with any additions, omissions or substitutions directed to be made by these or any other amending regulations, but with a footnote in each instance referring to such amending regulations; and the principal regulations so printed may be cited as the Public Health (Preservatives, &c., in Food) Regulations.

Given under the Official Seal of the Minister of Health this Tenth day of December, in the year One thousand nine hundred and twenty-six.

(L.S.)

R. B. CROSS,  
*Assistant Secretary, Ministry of Health.*

The Minister has issued the following Circular to the Clerks of Authorities (England and Wales) administering the Sale of Food and Drugs Acts.

PUBLIC HEALTH (PRESERVATIVES, &c., IN FOOD) AMENDMENT  
REGULATIONS, 1926.

CIRCULAR 751.\*

SIR,

1. I am directed by the Minister of Health to refer to Circular 606, dated the 11th August, 1925, and to forward for the information of the Authority a copy of the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1926, which postpone the operation of the Public Health (Preservatives, &c., in Food) Regulations, 1925, so far as certain foods are concerned, and make certain minor alterations in those Regulations.

2. The dates on which the principal Regulations as now amended will come into operation are as follows:—

- |  |         |                   |
|--|---------|-------------------|
| (1) All foods except those specified below   | .. .. . | 1st January, 1927 |
| (2) Bacon, ham, egg yolk and articles of food containing preservative necessarily introduced by the use in their preparation of preserved margarine  | .. .. . | 1st July, 1927    |
| (3) Butter, cream and articles of food containing preservative necessarily introduced by the use in their preparation of preserved bacon, preserved ham, preserved egg yolk or preserved cream | .. .. . | 1st January, 1928 |
| (4) Articles of food containing preservative necessarily introduced by the use in their preparation of preserved butter  | .. .. . | 1st July, 1928    |

3. A number of communications have been received from various trade interests, representing that, owing to the exceptional industrial conditions or other causes, it has not been possible for retailers completely to clear their old stocks before the date on which the Regulations operate. In view of the time which has elapsed since the original Regulations were made and the desirability of avoiding further elaboration in regard to the dates of their application to particular commodities, the Minister has not felt justified in acceding to the requests for further postponement. Local Authorities, however, will probably consider it desirable to refrain from instituting legal proceedings during the next few months where they are satisfied that reasonable efforts have been made to clear old stocks and that further consignments will conform with the Regulations.

4. The arrangements with the Commissioners of Customs and Excise which are referred to in the second paragraph of Circular 606 have now been so modified as to provide that it will normally be left to Local Authorities to enforce the Regulations as regards imports of fresh fruit (not including pulp) in addition to the articles (meat and fish and their products) specified in that paragraph.

\* H.M. Stationery Office. Price 1d. net.

5. In pursuance of Article 3 of the Amendment Regulations arrangements are being made for the printing of the principal Regulations in the form in which they will operate as now amended. The Regulations so printed will be known as the Public Health (Preservatives, &c., in Food) Regulations, and copies will be obtainable in due course through any bookseller or directly from His Majesty's Stationery Office.

I am, etc.,

R. B. CROSS,

*Assistant Secretary.*

December 16, 1926.

---

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

---

### Food and Drugs Analysis.

**Colorimetric Determination of the Hydrogen Ion Concentration of Milk, Whey and Cream.** P. F. Sharp and T. J. McInerney. (*J. Biol. Chem.*, 1926, 70, 729-758.)—Previous work on the determination of the  $P_H$  value of milk is discussed, and particularly the dialysis and dilution methods. The colorimetric determinations on the hydrogen ion concentration of the diffusate from milk agreed with the electrometric determinations made on the original milk, because the dilution error was compensated for by an indicator error. Brom-thymol blue and brom-cresol purple were used for the range. If this compensation is assumed, the dialysis method is fairly satisfactory for colorimetric determinations of the  $P_H$  value of milk, and the colorimetric determination of the hydrogen ion concentration of the diffusate can be taken as being 0.03 to 0.04  $P_H$  greater (more alkaline) than the  $P_H$  of the original milk. Tables show the effect of dilution to 20 volumes on fresh milk, sour milk and artificially soured milk. As the milk sours and after reaching a  $P_H$  value of about 5.6, the decrease in acidity on dilution becomes less. The rate of decrease in the dilution factor with increasing acidity is the same for natural or artificial souring. The dilution factor (obtained by plotting  $P_H$  against log. of vol. of dilution and finding the difference in  $P_H$  of the original milk and of the 20 vol. dilution) is a function of the  $P_H$  of the original milk. These factors were plotted against the  $P_H$  of the 20 vol. diluted milk. Similar experiments were carried out on whey. A correct  $P_H$  determination of cream can be made electrometrically if the fat content of the cream is not too high. Thus the  $P_H$  value of 25 per cent. cream agrees with the  $P_H$  of skim milk; the  $P_H$  of 40 per cent. cream diluted with an equal vol. of water and corrected agrees with the skim milk dilution curve. The dilution method applied to cream did not lend itself to accurate colorimetric determinations due to the turbidity caused by large amounts of fat. For this colorimetric method, results of about the same accuracy as those obtained with milk should be obtained by separation of the skim milk, dilution of it to 20 volumes and application of the correction factor for milk. The dialysis method may be more accurate, but the dilution method is more generally useful. A method for the colorimetric determination of the  $P_H$  of milk, whey,

cream, powdered milk, evaporated milk and sweetened condensed milk, with the use of standard buffer solutions has been elaborated and is described, based on the application of correction factors for the effect on the  $P_H$  value of the dilution of the product with 19 volumes of distilled water in order to reduce the turbidity and to make it possible for light to pass through the solution. It gives results usually correct within  $0.1 P_H$ , the average error being about  $\pm 0.06 P_H$ .

P. H. P.

**Use of Sodium Nitrite in the Curing of Meat.** R. D. Kerr, C. T. N. Marsh, W. F. Schroeder and E. A. Boyer. (*J. Agric. Res.*, 1926, 33, 541-551.)—The function of sodium nitrite in the curing of meat is to preserve the colour, and it may be successfully used in place of sodium or potassium nitrate, since these only function in so far as they are reduced to nitrite. Varying with the different processes in use, 0.25 to 1 oz. of sodium nitrite is sufficient to fix the colour in 100 lbs. of meat, and a shortening of the period of curing is brought about by its use.

D. G. H.

**Cellulose Sausage Casings.** W. F. Henderson and H. E. Dietrich. (*Ind. Eng. Chem.*, 1926, 18, 1190-1194.)—A satisfactory substitute for the usual sausage skins (animal intestines) has been devised by the authors, the material used consisting of cellulose derived from purified cotton linters. The viscose process was employed for making the cellulose into tubular form. The viscose solution was pressed through annular orifices into ammonium sulphate baths; after passing through acid and washing baths the cellulose tubes were dried by air in canvas casings. Softeners or lubricants were not employed. The tubes were filled while dry with the sausage meat, and immediately after filling the casings absorbed moisture from the meat and became soft and pliable. The cellulose casings are clean and have many advantages from a sanitary or hygienic point of view.

W. P. S.

**Behaviour of Different Starches towards Dyestuffs and Iodine. Part II.** J. Huebner and K. Venkataraman. (*J. Soc. Dyers & Col.*, 1926, 42, 327-332.)—The action of iodine vapour furnishes a ready and moderately reliable method of distinguishing individual starches. When placed under a bell-jar with a watch-glass containing resublimed iodine, maize starch becomes violet in 30 minutes and intense blackish-violet in 3 hours; rice starch turns pale violet in an hour and blackish later; potato starch is affected more slowly and becomes yellowish-grey at first and brownish-khaki in 24 hours; wheat starch slowly turns pale violet and is dull medium violet after 24 hours; sago starch becomes grey and then mole colour, and tapioca starch changes very gradually to a faint drab colour. It seems likely that the extent to which iodine vapour is absorbed is due partly to the alkalinity of the mineral ingredients of the starch. Colour effects similar to those given above are obtainable more rapidly by grinding the starches with solid iodine. Rice starch, with the smallest granules among the starches examined, absorbs

the largest proportion of iodine from its solution in aqueous potassium iodide, and potato starch, with the largest granules, absorbs the least, but the order of absorption for the other starches is not quite that of the magnitudes of the granules.

When starch is dyed with methylene blue (*cf.* ANALYST, 1926, 51, 351), the granules are dyed right through, but the colour is more intense at the edges, so that the shape of the granules is more clearly marked than in the original starches; further, the rings of potato starch are rendered sharper. Under polarised light the dyed starches exhibit no particular distinguishing feature.

With a mixture of starches, identification of the constituents by means of the microscope is considerably simplified by dyeing the mixture with a basic dyestuff without mordant. The different starches are dyed different shades and may be distinguished with comparative ease, and in a uniform mixture, the percentages of the various components may be determined approximately by counting.

T. H. P.

**Colour Reactions of Flours.** A. Piedallu. (*Ann. Falsif.*, 1926, 19, 481-482.)—Flours may be separated by the following reaction into two groups according to whether the colour reaction is positive or not. About 1 c.c. of the flour is treated with 70-90 per cent. alcohol to which has been added 2.5 per cent. of iron-free hydrochloric acid, and the mixture warmed, the reaction being considered at an end after 6 minutes. In the case of buckwheat the solution is an intense garnet colour and the flour violet; sorghum, a rose colour slightly violet; barley, "old rose"; vetch, bright violet, or "old rose"; cow wheat, greenish-blue; and corn-cockle, orange-yellow; wheat, rye, maize, rice, oat, canary grass, and millet give no definite colour reactions.

D. G. H.

**Notes on Sugar Determination.** M. Somogyi. (*J. Biol. Chem.*, 1926, 70, 599-612.)—The effect of variations of alkalinity upon the reduction values in the system—glucose and alkaline copper solution—has been studied. A series of nine copper reagents was prepared, in all of which Rochelle salt was used instead of tartaric acid; the reagent of highest alkalinity contained 40 grms. of sodium carbonate per litre, and the other eight solutions were made up with buffer mixtures which contained varying amounts of sodium carbonate and bicarbonate. Results show that comparatively small changes in alkalinity (and thus in  $P_H$ ) produce considerable differences in reduction values. From the fairly close parallelism of two curves given ("apparent"  $P_H$  values plotted against mgrm. of copper reduced by 1 mgrm. of glucose) it is seen that the effect of variations in alkalinity is much the same for different concentrations of glucose. The highest reduction values are furnished by reagents of  $P_H = 9.40$  to  $9.55$  or  $\frac{[Na_2CO_3]}{[NaHCO_3]} = \frac{7}{15}$  and  $\frac{2}{3}$ . This explains the discrepancies in sugar determinations by copper-reduction methods. A modification of the Shaffer-Hartmann (*J. Biol. Chem.*, 1920-21, 45, 365) carbonate and tartrate copper reagent is offered which (1) has a more constant degree of alkalinity, (2) gives higher reduction values, and (3) extends the usefulness of the

method to lower concentrations of glucose (blood sugar values 0.020 per cent.). The composition of the modified reagent is as follows:—

Final concentration.		Grms. per litre.	Final concentration.		Grms. per litre.
0.026 M	Copper sulphate (crystalline) ..	6.5	0.023 N I <sub>2</sub> {	Potassium iodide	10
0.06 M	Rochelle salt .. .. .	12		.. iodate	0.80
0.2 M	Sodium carbonate (anhydrous)	20	0.1 M	.. oxalate	18
0.3 M	.. bicarbonate .. .. .	25			

The Rochelle salt, sodium carbonate and sodium bicarbonate are dissolved in about 500 c.c. of water, and into this the copper sulphate, dissolved in about 100 c.c. of water, is poured; the solution of the other constituents is then added, and the whole diluted to 1 litre. Only the potassium iodate must be weighed accurately to cgrm. An adaptation of the Shaffer-Hartmann method for 0.2 c.c. of blood is described, and attention is directed to a few technical details which may cause errors in determinations by these methods.

P. H. P.

**Distribution of Volatile Flavour in Grapes and Grape Juices.** J. W. Sale and J. B. Wilson. (*J. Agric. Res.*, 1926, 33, 301-310.)—The content of anthranilic acid ester and total volatile esters affords a measure of aroma in grapes and grape juices. The former may be satisfactorily determined by a modification of Mathewson's method whereby the steam distillate is treated directly, and the excess of nitrous acid after diazotising is destroyed by hydrazine sulphate. The colour formed on addition of sodium- $\alpha$ -naphthol-2-sulphonate and sodium carbonate is then proportional to the amount of anthranilic acid ester present, which in 84 samples of whole grapes (about 55 varieties) varied from 0.00 to 3.80 mgrms. per kilo. Total volatile esters are determined after titration of the volatile acids by adding excess of 0.1 N alcoholic potassium hydroxide solution, heating under a reflux condenser and titrating the excess of alkali with 0.1 N sulphuric acid. Volatile esters and acids in 50 samples (about 34 varieties) varied from 6 to 366 and 3 to 121 mgrms. per kilo., respectively. Anthranilic acid ester was not found in the fruit of *Vitis vinifera*. Volatile flavour is present in the pulp, as well as the skin, and nearly as much remains in the pomace as is expressed in the juices, but the ester tends to disappear from stored juices. D. G. H.

**Detection of other Fruit Wine in Grape Wine.** T. Röttgen. (*Chem. Zeit.*, 1926, 50, 858-859.)—None of the various methods yet proposed for the detection of other fruit wine in grape wine, including microscopic examination of the centrifuged residue for starch granules, yields definite results. The following procedure has, however, proved satisfactory with all the sound white wines to which it has been applied. The wine is neutralised by addition of concentrated sodium hydroxide solution (1:1), and 17 c.c. are then treated in a glass-stoppered 25 c.c. cylinder with 3 c.c. of a mixture of 85 vols. of 5 per cent. neutral copper acetate solution with 15 vols. of 10 per cent. ammonia solution; the liquid is mixed by tilting the cylinder once only. Grape wine does not alter the blue colour of the reagent, but the presence of 20 or, in some cases, 10 per cent. of cider or perry results in a



distinct greenish tinge. In doubtful cases, comparison with the colour given by a genuine wine is useful. The reagent should be kept in brown dropping bottles, and should not be more than 14 days old.

T. H. P.

**Sulphur Dioxide and the Behaviour of Bottled White Wines.** J. Dubaquié. (*Ann. Falsif.*, 1926, 19, 459-462.)—The cloudiness which so often develops in bottled white wines and causes large losses in the industry appears to be due in large measure to the action of substances present in the wines, notably sulphur dioxide, on the glass of the bottles. Aluminium is acted on by very dilute sulphurous acid, and the aluminium sulphite forms insoluble pectates from pectin bodies, which on oxidation in feebly acid medium may become soluble (note absence of cloudiness in aerated wines). It was found on bottling the same wine in ordinary glass bottles and in bottles the glass of which contained only traces of iron and aluminium, that in the case of the latter no trouble was experienced, whilst a proportion of samples in the ordinary bottles showed sediments. More generalised experiments are required, and it is probable that the case is much more complicated than this. Pectic materials can only be withdrawn from the wines at the expense of the flavour.

D. G. H.

**Determination of Santonin in Santonica.** Eder and W. Schneider. (*J. Suisse de Pharm.*, 1925, 63, 405-409, 421-425, 433-439, 453-458; *J. Pharm. Chim.*, 1926, 118, 457-458.)—Ten grms. of the fine powder of santonica are shaken in a 150 c.c. flask for half-an-hour with 100 grms. of benzene, the mixture filtered through a 18 cm. diam. paper, and 81 c.c. of the resulting solution completely distilled. The cooled residue is treated with 40 c.c. of 15 per cent. (by weight) alcohol, the mixture boiled for 15 minutes beneath a reflux condenser, and the hot solution filtered through cotton wool. The cotton and flask are washed with hot 15 per cent. alcohol, and, after the addition of 0.1 gm. of kaolin, the liquid is boiled for another 15 minutes beneath a reflux condenser, filtered hot into a weighed flask and left for 24 hours in the dark, with occasional shaking, when the santonin will have crystallised. After the flask has been weighed the contents are filtered, the flask and crystals washed with cold water, both dried at 100° C. and weighed, and a solubility correction of 0.006 gm. for every 10 c.c. of alcoholic extract made, the weight of santonin corresponding to 8 grms. of santonica being thus obtained. Santonin should be present in excess of 0.45 per cent., and, where a proof of its absence in a drug is sought, from 1.5 to 2 per cent. should be added to the sample before making the determination.

D. G. H.

**Determination of Cantharidine in Cantharides.** R. Eder and W. Schneider. (*Schweiz. Apoth. Ztg.*, 1925, 63, 229, 245; *Pharm. Weekblad*, 1926, 1282.)—As a modification of the method of the Swiss Pharmacopœia (IV), 10 grms. of powdered cantharides are heated under a reflux condenser on the water-bath for 30 minutes with 100 grms. of benzene and 1 gm. of 25 per cent. hydrochloric acid. The cooled liquid is filtered, and 5 grms. of the solvent removed from 81 grms. of the filtrate (corresponding to 8 grms. of the powder) by distillation,

and the remainder by means of a current of dry air below 60° C. To the warm residue are added 100 c.c. of a mixture containing 19 parts of petroleum spirit and 1 part of absolute alcohol, and the crystals are filtered off on a wad of cotton-wool, washed repeatedly with 5 c.c. of the mixture till the filtrate is colourless and dissolved in 2 to 3 c.c. of chloroform. This is removed in a current of dry air, and the cantharidine weighed after it has stood 12 hours in a desiccator. A weight of 0.064 grm. corresponds to 0.8 per cent. of cantharidine in the drug; the m.pt. is 212° C.

J. G.

**Detection of Codeine and Formaldehyde.** J. Aloy and A. Valdiguié. (*J. Pharm. Chim.*, 1926, 118, 390-393.)—Codeine may be detected by dissolving a little of the alkaloid in 3 to 4 c.c. of pure sulphuric acid, and adding 2 drops of a very dilute solution of iron or uranium acetate and 1 drop of dilute formaldehyde. After leaving the mixture for 2 minutes and shaking it gently a blue coloration forms in the presence of as little as 0.00003 grm. of codeine. The hydrochlorides of apocodeine, acetyl morphine and heroine give no coloration, whilst morphine produces a purple colour, but the reaction is not so delicate as with codeine. In the presence of other organic substances giving colours with sulphuric acid the codeine must first be separated. For example, syrup of codeine may be extracted with a few c.c. of chloroform after rendering the solution alkaline with sodium carbonate.

*Formaldehyde*.—To 3-4 c.c. of pure sulphuric acid are successively added 2 drops of the iron solution, a few drops of a 1 per cent. alcoholic solution of codeine, and 1 or 2 drops of the solution under examination, and, after standing for 1 to 2 minutes, the mixture is gently shaken; an intense blue colour then indicates the presence of formaldehyde. A thousandth of a mgrm. may thus be detected, but if the formaldehyde solution is too concentrated, a green colour results. The reaction is positive for condensation and combination products such as trioxymethylene, paraformaldehyde, tetramine, hexamethylene, citarine, creosoforn, helmitol, etc. Hexamethylene may thus be detected in the urine of patients taking urotropine. Formaldehyde and urotropine may be detected in foods such as wines and milk, but solid materials such as butter should be first extracted with water.

D. G. H.

**New Colour Reaction for Procaine and some other Local Anaesthetics and its Application to the Determination of Procaine.** E. R. Riegel and J. F. Williams.

(*J. Amer. Chem. Soc.*, 1926, 48, 2871-2878.)—Addition of a few drops of hydrochloric acid, of sodium nitrite, and of concentrated ammonia solution to a solution containing about 1 mgrm. of procaine hydrochloride per c.c. results in the development of an intense yellow coloration. Tutocaine, butyn, butesin, propaesin, benzocaine, and orthoform also give this reaction, which is, however, not obtained with cocaine, tropacocaine, alypine,  $\beta$ -eucaine, apothesine, benzyl alcohol, stovaine, quinine, and phenacaine. Epinephrine gives the same coloration very slowly; saligenin yields a yellow, and morphine and apomorphine a red, coloration with the hydrochloric acid and nitrite alone, the colour being changed to mahogany brown by ammonia in the case of apomorphine. A number of

alkaloids, and also acetanilide, lactose and corn sugar, although they give no coloration, either before or after addition of ammonia, affect the delicacy of the test, and thus interfere with it when used for the determination of procaine, etc.

For the determination, an amount of substance representing 0.01 to 0.015 grm. of procaine is dissolved in 10 c.c. of water in a 100 c.c. flask, the solution being mixed with 0.5 c.c. of 10 per cent. hydrochloric acid, and 1 c.c. of 2 per cent. sodium nitrite solution, and afterwards with 1 c.c. of concentrated ammonia solution. When the turbidity which develops reaches a maximum, the volume is made up to 100 c.c. with water. Of this stock solution, 1, 1.25, 1.5, 2 and 2.5 c.c. are pipetted into 50 c.c. Nessler tubes and each made up to the mark, and the series compared with a potassium dichromate tube prepared by diluting 8.5 c.c. of 0.1 per cent. dichromate solution to 50 c.c.; this tube corresponds with a total content of 0.25 mgrm. of procaine. The method gives results accurate to within about 10 per cent.

T. H. P.

## Biochemical, Bacteriological, etc.

**Value of the Saponins as Foam-producing Materials. R. Mand.** (*Chem. Ztg.*, 1926, 50, 850.)—An evaluation for saponin is given by Kofler (*ANALYST*, 1922, 47, 403; 1924, 49, 239) as the quotient, haemolytic index—foam number. This value should not exceed unity, 0.5 being the optimum. The author points out that his product "Aphrogen" has been assigned too low an evaluation by this method. A similar product "Spumagen" is described, and the table shows a comparison of its properties with those of other saponins.

	Haemolytic index.	Foam number	Poison Froth
Guaiacum saponin. Merck. .. ..	660	28,500	0.023
Sapotoxin, Merck. .. ..	30,000	20,000	1.5
Sapindus saponin. } .. ..	28,000	16,700	1.7
Hoffman-La Roche }			
Horse-chestnut saponin. Merck. ..	10,000	3,300	3.0
Sap. pur. albiss. Merck. .. ..	25,000	2,500	10.0
Quillaia saponin. .. ..	32,000	10,000	3.2
Spumagen Mand. .. ..	2,000	3,700	0.5

Subcutaneous injection experiments show that the relative haemolytic and toxic effects of different saponins may differ considerably, and it is suggested that as a means of evaluation, the quotient, haemolytic index  $\times$  toxicity/foam number, be used. If the toxicity of "Spumagen" is unity, that of quillaia saponin is 80.

J. G.

**Hydrolysis of Corn (Maize) Starch by Commercial Pancreatin. J. H. Walton and H. R. Dittmar.** (*J. Biol. Chem.*, 1926, 70, 713-728.)—Since the hydrolysis of potato starch proceeds more rapidly and completely than the hydrolysis of corn starch, investigations were made to find the most favourable conditions for the hydrolysis of corn starch. A definite amount of pancreatin,

usually dispersed in a definite amount of water, was added to the starch solution at 40° C., from which portions were withdrawn from time to time for analysis. Hydrolyses were made on 98 c.c. of a 2 per cent. (dried) starch solution. The potato starch is hydrolysed more rapidly than corn starch by pancreatin, owing to a difference in the chemical nature of the two, for corn starch was found to contain a material of a hemicellulose nature which was very slowly hydrolysed by the enzyme. The enzymatic action was found to stop when the maltose content was 85 per cent. of the total weight of the starch, as found by Sherman and his co-workers. The rate of conversion of corn starch was not increased after the starch had been rendered soluble according to Lintner (*J. prakt. Chem.*, 1886, **34**, 378), autoclaved dry, autoclaved in solution, frozen, or ether-extracted. In an attempt to increase the speed of conversion of corn starch by the substitution of other salts besides the disodium phosphate and sodium chloride, potassium and ammonium chlorides were found to act as well as the sodium chloride, whilst sodium citrate, sodium succinate and sodium ammonium hydrogen phosphate could be used in place of the disodium phosphate. None of these salts increased the rate of hydrolysis more than the sodium chloride and phosphate except sodium citrate, which, when used with the sodium chloride, showed a slightly more favourable effect.

P. H. P.

**Determination of Hydrogen Ions in the Blood with the Aid of the Duboscq Colorimeter.** J. F. McClendon, S. Russell and E. Tracy. (*J. Biol. Chem.*, 1926, **70**, 705-711.)—The Duboscq "biological colorimeter," with slight modifications, has been adapted for the determination of hydrogen ions in blood plasma. For this work an indicator was necessary that shows change only in intensity of colour with degree of dissociation, and not a mixture of two colours, such as is the case with phenol red. The best indicator found was ortho-chrom-T, but para-nitro-phenol, a rather strong precipitant of the plasma proteins, can also be used. In 10 c.c. of alcohol, 0.1 grm. of ortho-chrom-T is dissolved, and this is mixed with 90 c.c. of distilled water and kept in a bottle with a dropping pipette. The two precautions necessary for the determinations are: (1) to guard against loss of carbon dioxide from the blood plasma and (2) to secure absolute symmetry in the optical arrangements on both sides of the colorimeter. The first is overcome by the use of a cup with a fused-on glass bottom and a removable cover which fits tightly on the liquid. For micro determinations a cup with a side neck is used with the Buerker colorimeter. Barium hydroxide is added to the second cup to give the same amount of cloudiness as the indicator gives with the proteins of the plasma. Full experimental details are given. The percentage dissociation is obtained experimentally, and the  $P_H$  is found by means of a chart given which was made from work on ox serum at 27°. A second diagonal is drawn on the chart for the case of para-nitrophenol. Since this indicator is rather pale, a few drops of a 1 per cent. aqueous solution are used. If there is any change in temperature, or salt content, or any variation in the indicator, the method should be re-standardised and a new diagonal drawn.

P. H. P.

**Colour Tests Suggested for Vitamin A.** O. Rosenheim and T. A. Webster. (*Lancet*, 1926, 211, 806-807.)—Of the two colour reactions recently brought to notice as associated with the presence of vitamin A, either would be suitable for colorimetric application if its specificity for that vitamin were established. In the first, discovered by Rosenheim and Drummond (*Biochem. J.*, 1925, 19, 753), a transient blue colour is developed by the addition of arsenic chloride, or antimony chloride (Carr and Price, *Biochem. J.*, 1926, 20, 497) to cod-liver oil, and in the second, described by Fearon (*Biochem. J.*, 1925, 19, 888) a permanent red colour is produced by pyrogallol in the presence of trichloroacetic acid and an oxidising agent. The authors have applied these tests to different oils of which they have also tested the growth-promoting power. It is shown that the two colour reactions are due to two entirely different chromogenic substances, and Fearon's method has no value for the purpose intended. Of the liver oils, only fish-liver oils give Fearon's reaction. Oils which gave Fearon's reaction but not the  $\text{AsCl}_3$  reaction were not growth-promoting, and some growth-promoting oils did not give the pyrogallol reaction. The possibility of the arsenic chloride test being specific for vitamin A still remains open. When mixed with an active sample of cod-liver oil, an oil which gave a strong peroxide reaction and was inactive in the growth-test, rapidly destroyed the chromogen of the  $\text{AsCl}_3$  reaction. Thus the peroxide reaction requires consideration in further work. P. H. P.

## Toxicological and Forensic.

**Poisoning by Mercury Vapour.** L. M. Dennis. (*Ind. Eng. Chem.*, 1926, 18, 1205.)—Instances are mentioned where workers with apparatus containing mercury (pumps, manometers, valves, troughs, etc.) have suffered from mercurial poisoning. In most cases the effects attained serious gravity only after several years' exposure to the air containing mercury. The atmosphere of a laboratory where the apparatus mentioned was installed contained up to 0.01 mgrm. of mercury per cb. m. of air. At ordinary temperatures air saturated with mercury contains about 12 mgrms. of the metal per cb. m., but persons who had worked for one or two years in the laboratory suffered severely from mercurial poisoning. Mercury poisoning has also been caused by silver-amalgam dental fillings.

W. P. S.

**Acridness and Toxicity of Cruciferous Seeds and Oil Cakes.** G. Jorgensen. (*Ann. Falsif.*, 1926, 19, 454-459.)—Seeds of *Brassica juncea* (probably identical with *Sarepta* mustard) and other seeds giving rise to essential mustard oil are to be regarded as toxic. Acridness and development of allyl mustard oil may be gauged by macerating 1 grm. of the sample and some powdered white mustard in water for 1 hour in a closed flask, and if the odour is not then frankly acrid the sample is regarded as nearly free from acrid material. Also, 15 grms. of sample are left in water for 3 days, and the odour noted twice a day, when samples developing allyl mustard oil in considerable quantity will smell acrid on the third day, whilst others will have lost any such smell before that time. It is useful to determine

the percentage of nitrogen in the thiosinamines of oil cakes, since it runs as high as 23·6 per cent. in oil cakes made from *B. juncea*, whilst in cakes free from these seeds it never exceeds 21·1 per cent. (*cf.* ANALYST, 1909, 34, 489). Six samples of colza cake found to be rich in *B. juncea* seeds, and which had been toxic to animals eating them, contained 22·5–22·8 per cent. of thiosinamine nitrogen, and developed 0·79–0·98 per cent. of essential mustard oil. Any samples containing over 22·0 per cent. of thiosinamine nitrogen are to be regarded with suspicion, even if only 0·35 per cent. of allyl mustard oil is liberated in the presence of myrosin. Thiosinamines containing about 22·5 per cent. nitrogen were never found to be so lid in the air, whilst those containing over 23·5 per cent. had melting points from 64 to 73° C.

D. G. H.

## Water Analysis.

**Volumetric Method for the Determination of Magnesium in Industrial Waters.** C. Belcot. (*Bull. Soc. Chim.*, 1926, 39, 1483–1485.)—Pfeifer's method for determining magnesium in presence of calcium salts (*Z. angew. Chem.*, 1902, 16, 199), which gives results sufficiently accurate for industrial purposes, is carried out as follows:—Ten c.c. of the water are heated and titrated with 0·1 *N* hydrochloric acid in presence of alizarine, and the liquid, now free from free carbonic acid, is introduced into a 200 c.c. flask, together with boiling distilled water. After addition of a measured excess (25 to 50 c.c.) of standard calcium hydroxide solution, the volume is made up to 205 c.c., and the flask closed with a rubber stopper and shaken vigorously. After an interval of a few minutes the liquid is cooled and filtered through a large pleated filter. The excess of calcium hydroxide in 100 c.c. of the filtrate is determined by titration with acid in presence of phenolphthalein. The quantity of calcium hydroxide used in the precipitation of the magnesium salts is thus found by difference; 1 c.c. of 0·1 *N* calcium hydroxide corresponds with 0·002 grm. of MgO.

T. H. P.

## Organic Analysis.

**Determination of Carbon in Dilute Organic Liquids.** O. Kauffmann-Cosla. (*Bull. Soc. Chim.*, 1926, 39, 1485–1492.)—The carbon in a solution such as urine may be determined by a modification of the ordinary method of combustion in presence of cupric oxide in a current of oxygen. Use is made of a quartz combustion tube, which not only withstands the sudden changes of temperature accompanying the evaporation of the large volume of water, but also admits of more intense heating than a glass tube. The liquid to be analysed is absorbed by asbestos in a small Jena glass tube, which is closed at one end, and has a number of perforations at the other and contains also coarsely ground copper oxide wire. Two calcium chloride tubes are used to retain the water driven over in the gases from the combustion, that branch of the first which is the nearer to the combustion tube being furnished with a small bulb cooled by moistened cotton wool to condense most of the water vapour. Test determinations with solutions of dextrose, alcohol, and urea, together with chloride, sulphate and phosphate, gave results accurate to the same degree as the combustion of solid organic compounds.

T. H. P.

**Colour Test for Cyanic Acid.** W. R. Fearon. (*J. Biol. Chem.*, 1926, 70, 785-792.)—A colour reaction of considerable delicacy has been devised which will show the presence of cyanate in the silver precipitates obtained from the zymolysis of urea. To 5 ml. of water, 2 to 5 drops of a 6 per cent. alcoholic solution of benzidine are added and a couple of drops of a 6 per cent. solution of copper acetate. This is mixed, and the cyanate solution, which should be neutral or faintly acid, is added. A purple colour develops and rapidly changes into a sepia precipitate, which soon separates from the solution. The test is definitely positive with less than 0.1 mgrm. of potassium cyanate; but is capable of a greater degree of delicacy. Acids cause decomposition of the compound and hydrolyse the cyanate. Alkalis inhibit the formation of the coloured compound. Cyanides, thiocyanates, thio-sulphates, iodides and bromides form dense coloured precipitates with the benzidine-copper reagent; sulphates precipitate the benzidine; for this reason copper acetate is used. The test is capable of a gravimetric application, as the precipitate can be filtered off, washed with water and alcohol and dried. The compound is sparingly soluble in the commoner neutral organic solvents. It dissolves, with decomposition, in pyridine and in acetic acid, and is readily hydrolysed by dilute mineral acids, the cyanate being converted into the ammonium salt of the acid. It appears to have the formula  $\text{Cu}(\text{OCN})_2\text{Bz}$ .

P. H. P.

**Volumetric Determination of Hydroquinone.** I. M. Kolthoff. (*Rec. Trav. Chim. Pays Bas*, 1926, 45, 745-752.)—The titration of hydroquinone with iodine and with dichromate, both by the usual application of colour indicators and potentiometry, was studied. *Iodine titration.*—The best results are obtained in slightly acid solution. The neutral 0.1 N solution (25 c.c.) is treated with 0.1 to 1 c.c. (not more) of 4 N acetic acid and about 20 c.c. of 2 N sodium acetate. A measured excess of iodine is added, and this is titrated back with thiosulphate in presence of starch. In the titration of 0.01 N solutions, not more than 0.2 c.c. of the acetic acid should be present. The direct titration with iodine and starch is not satisfactory, but in the potentiometric method a sudden sharp break occurs at the equivalence point. The electrodes are platinum gauze and the normal calomel electrode; 50 c.c. of the hydroquinone solution are treated with 2 drops of 4 N hydrochloric acid and 1 to 2 grms. of sodium bicarbonate. The iodine is added from a burette while the liquid is being stirred. *Dichromate method.*—The solution (25 c.c.) is acidified with 4 N sulphuric or hydrochloric acid (15 to 20 c.c.); 0.1 to 0.2 c.c. of a 0.1 per cent. solution of diphenylamine serves as indicator. 0.1 N dichromate solution is run in at 40° to 60° C.; the liquid turns yellow at first, then dirty green-brown. Near the end the dichromate is added very slowly (a drop each 10 seconds). The end-point is given by a change of colour towards violet. The process gives accurate results in presence of phenols and cresols, where the iodimetric method fails. If the liquor has a dark colour the end-point must be ascertained by potentiometric measurement. The platinum gauze electrode must be heated to redness after each titration because of the depolarising action of quinone. The potential is soon constant during titration; near the end 2 to 3 minutes must elapse before the reading is constant, but when a small excess

of dichromate is present this takes place almost immediately. The liquid to be titrated (50 c.c.) is acidified with 25 c.c. of 4 *N* sulphuric acid. The results are also accurate in presence of phenols. W. R. S.

**Fatty Oil of Sweet Clover Seed.** B. A. Dunbar and C. F. Wells. (*J. Oil & Fat Ind.*, 1926, 111, 382-385.)—The composition of the seed of *Melilotus albus*, a biennial clover, grown at South Dakota, was found to be:—Moisture, 6.58; ethereal extract, 5.26; protein, 35.17; crude fibre, 11.15; ash, 3.46; and nitrogen-free extract, 48.38 per cent. The constants of the extracted oil were as follows:—Sp. gr. at 25° C., 0.9513;  $n_D^{25}$ , 1.4838; free fatty acids, 4.08 per cent.; saponification value, 203.3; iodine value (Hanus), 142.5; unsaponifiable matter, 3.05 per cent.; glycerol, 11.11 per cent.; fatty acids, 86.9 per cent.; Reichert-Meissl value, 3.45; neutralisation value of unsaturated acids, 198.9; of saturated acids, 216.3; iodine value (Hanus) of unsaturated acids, 147.16; of saturated acids, 68.05; mean molecular equiv. of unsaturated acids, 282.1; of saturated acids, 259.75; acetyl value, 43.13. The oil is regarded as a drying oil. D. G. H.

**Nitrogen in Leather.** R. W. Frey. (Committee Report, *J. Amer. Leather Chem. Assoc.*, 1926, 583.)—The chief point in this report is whether the ammonia distilled over in the Kjeldahl process should be absorbed by standard hydrochloric acid or by a strong solution of boric acid which need not be standard. Fifteen samples of various leathers were examined by means of these two modifications, sodium alizarin sulphonate and methyl orange, respectively, being used as indicators. In thirteen cases the results agree within 0.1 per cent. or less, the average of all with boric acid being 0.05 per cent. higher than with hydrochloric acid. In the author's opinion this small discrepancy could be reduced by using bromphenol-blue instead of methyl orange. R. F. I.

**Leather Analysis.** G. Powarnin and I. Schischiroff. (*Coll.*, 1926, 269; *J. Inter. Soc. Leather Trades Chem.*, 1926, 10, 392.)—The authors draw the following conclusions:—In the determination of soluble substances by the alcohol-water method, considerably more tans are found when the alcohol treatment precedes that with water than when water is used first. The durability of dry leather appears to be proportionate to the degree of tannage; the higher this figure, the greater the durability. The wearing test by rotation of the sample against sand-paper, as described, gives a higher result than a test in which the sand blast is used. Samples must be dry. The resistance to wear appears to be the opposite of the resistance to tearing. In considering the influence of sulphuric acid on a leather, the proportion of soluble salts present, must be taken into account. The authors suggest a new constant—the "homogeneity of tannage"—based on the nitrogen content, or on the degree of tannage, of different layers. R. F. I.

## Inorganic Analysis.

**Direct Determination of Nitrogen in Lighting and Heating Gas.** W. Steuer. (*Chem. Ztg.*, 1926, 50, 860.)—The following procedure, which occupies 20 to 25 minutes, gives results as accurate as those obtained by the Dumas method in a much longer time. Into one Dumas burette are introduced exactly 100 c.c.



of the gas, and into the other sufficient oxygen to leave a remainder of 5 to 15 c.c. after combustion. Electrolytic oxygen is the most suitable, but if only Linde oxygen is available, its nitrogen content must be determined by a blank experiment. About 80 or 90 c.c. of oxygen will be required, so that it is well to introduce about 100 c.c., to connect with the quartz capillary tube, to expel the air from this by means of some of the oxygen, and then to join the free end of the capillary with the burette containing the gas. The cock is opened and the gases mixed, the main bulk of the hydrogen, carbon monoxide, and heavy hydrocarbons being first burnt by heating the palladium in the capillary with a small Bunsen flame. Finally, the heating is continued with the full flame until the volume no longer changes. From the residual mixture of nitrogen, carbon dioxide and oxygen, the last two are dissolved in fresh alkaline pyrogallol solution; if an old solution is used, any small amount of carbon monoxide which may be formed should be absorbed before the volume of the nitrogen is measured.

T. H. P.

**Potassium Bi-iodate as a Standard Substance in Alkalimetric and Iodimetric Titrations.** I. M. Kolthoff and L. H. van Berk. (*J. Amer. Chem. Soc.*, 1926, 48, 2799-2801.)—Potassium bi-iodate, prepared by Shaffer and Hartmann's method (*J. Biol. Chem.*, 1920, 45, 376), remains unchanged after crystallisation from water, and serves well for the standardisation of thiosulphate and, more particularly, alkali, its equivalent weight being high and iodic acid acting as a very strong acid which may be used with all indicators showing a colour change between dimethyl yellow and phenolphthalein.

T. H. P.

**Acidimetric Determination of Nickel as the Nickeldicyandiamidine Salt.** P. Fluch. (*Z. anal. Chem.*, 1926, 69, 232-243.)—Nickel may be separated from solutions containing it by precipitation as nickel dicyandiamidine by means of dicyandiamidine sulphate in the presence of ammonia. The precipitate, which has the formula  $\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ , is washed with alcohol on an asbestos or glass filter, or dried, to remove the ammonia. The drying process also removes the two molecules of water. The precipitate is then titrated (the filter may be conveniently included) with 0.2 *N* hydrochloric acid, with 1 to 2 drops of a 0.2 per cent. solution of methyl red in alcohol solution as indicator. One atom of nickel is equivalent to 4 molecules of acid. The results obtained show close agreement with those obtained by the gravimetric nickel dimethylglyoxime method, but, in general, are a little low. For alloys containing copper, this element must first be removed by hydrogen sulphide, as it is also precipitated by the reagent. It is suggested that the method may be extended to the determination of copper. For nickel-chrome steels the iron may be removed by the sodium acetate method, or else treated with Rochelle salt. The former method gives results in better agreement with the gravimetric method, and a maximum deviation of 0.05 per cent. is recorded.

J. G.

**Two Sources of Error in the Electrolytic Determination of Nickel in the Presence of Iron.** C. Marie and J. Berthelot. (*Compt. rend.*, 1926, 183, 793-795.)—In the electrolytic separation of nickel from an ammoniacal solution

in the presence of iron, two sources of error exist :—(1) The hydrated iron sesquioxide adsorbs some of the nickel ; (2) it may also be reduced to iron at the cathode and be deposited with the nickel. The errors occur in solutions containing large and small quantities of nickel, respectively, and, under certain conditions, balance one another. The former error is reduced by the addition of magnesium, which replaces the adsorbed iron and converts the negative error into a small positive error, owing, possibly, to a trace of magnesium in the deposit. The second error is obviated by the use of a diaphragm of filter paper to protect the cathode. For a solution containing 20 per cent. of nickel the error was thus reduced from + 0.0086 to - 0.0004 grm. Where a diaphragm cannot be used, the nickel is deposited in the presence of magnesium, redissolved, and re-electrolysed.

J. G.

**Volumetric Determination of Chromium.** E. Müller and W. Messe. (*Z. anal. Chem.*, 1926, 69, 165-167.)—The solution of chromic sulphate is treated with 6 c.c. of 8 *N* sodium hydroxide and 0.5 grm. of chemically pure lead dioxide, and boiled for 10 minutes. The solution is filtered, and the residue thoroughly washed. Potassium iodide is added to the filtrate, which is then acidified with hydrochloric acid and titrated with thiosulphate (starch indicator). The precipitate of lead dioxide may be tested for chromate by being boiled for a minute with 4 *N* sodium hydroxide (4 c.c.) ; the liquid should not become yellow. If it does, it is filtered and added to the main filtrate. As the oxidation is carried out in alkaline solution, chlorides do not interfere.

W. R. S.

## Physical Methods, Apparatus, etc.

**Quantitative Determination of Mixtures of Two and Three Oils by means of their Separation Temperatures with different Solvents.** J. D. Jansen and W. Schut. (*Chem. Weekblad*, 1926, 23, 498-502.)—The separation temperatures of mixtures of certain oils with various amounts of aniline have been determined. Maximum values of the temperature-composition curves were obtained with about 80 per cent. of aniline, and the separation temperatures of the oils for these proportions are shown in the table :—

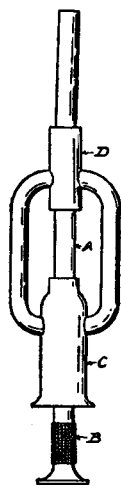
Oil.	Aniline. °C.	Acetone. °C.	<i>N</i> -propyl alcohol. °C.	Isobutyl. alcohol. °C.
Rape .. ..	37.5	19	27.5	16.5
Arachis .. ..	26	6-7	13	5
Olive .. ..	26	6	10	2
Cottonseed .. ..	19	1	8	2
Sesame .. ..	18	0	12	5
Soya bean .. ..	10	-8	9	4
Linseed .. ..	-6	—	6	5

Where a mixture of two oils with aniline is used, it is shown that the separation temperature isotherms for various proportions of the two oils should be straight

lines. In practice, a maximum deviation of  $-0.6^{\circ}$  C. was found with a mixture of 49.9 per cent. of arachis oil and 50.1 per cent. of rape oil. Similar data are also given for mixtures of three oils, and three-angle diagrams have been constructed to illustrate them. To obtain the proportions of the three oils present, the data derived from a second liquid have to be used in conjunction with those from aniline. The dimethyl and diethyl anilines, the *o*- and dimethyl-*p*-toluidines, benzene, toluene and nitrobenzene gave negative results. For acetone (in the proportion 2:3), the isotherms almost covered those of the aniline and oil system, whilst normal propyl and isobutyl alcohols gave separation temperatures for the different oils, which differed only slightly. The angles of intersection of the corresponding isotherms were consequently small. The use of another constant, such as the iodine value, refractive index, or specific gravity, in conjunction with the data for aniline is suggested instead, and future work on these lines is indicated.

J. G.

**Method for Differential Potentiometric Titration. D. A. MacInnes and P. T. Jones.** (*J. Amer. Chem. Soc.*, 1926, 48, 2831-2836.)—The advantages



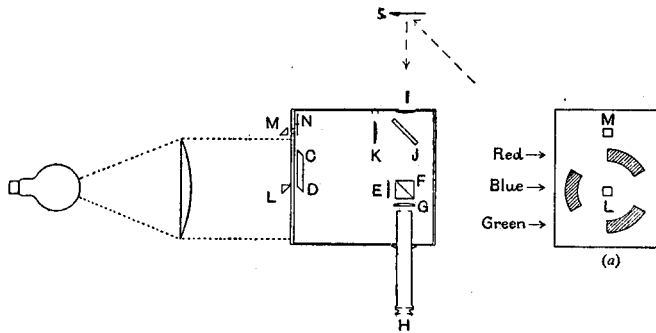
of Cox's method (*ANALYST*, 1925, 50, 581) may be retained and only one burette and one beaker used if a small amount of the solution surrounding one of the electrodes is kept temporarily from mixing with the rest of the solution until after each small increment of the titrating reagent is added. This may be done by means of the figured device, which consists of a central tube A carrying an electrode of platinum gauze B, this making contact with mercury on the inside of the tube. The cap C is connected with the guide tube D by means of glass rods, and C and D slide loosely on the inner tube A, a projection on which is ground to fit the lower edge of the cap C. When this apparatus is placed in a solution and the cap lowered, the solution about the electrode B is held in place and is not disturbed by vigorous stirring. During a titration the cap is lowered before each addition of reagent and the potential between B and the other electrode determined on a potentiometer.

Potentials measured in this way reach a sharp maximum at the end of the titration, and the method is capable of high accuracy and is applicable in every case in which potentiometric technique is possible.

T. H. P.

**Trichromatic Colorimeter Suitable for Standardisation Work. J. Guild.** (*Trans. Opt. Soc.*, 1925-6, 27, 106-129.)—Since all colour sensations are due to the admixture in various proportions of the spectrum colours, all colours are located in the colour field or area on a trichromatic colour chart bounded by the curved spectrum locus and the line joining its extremities. The shape, area and position of the field depend on the trichromatic primary colours used, and its area represents the limits within which the method may be used for colour matching. A colour of higher saturation (*i.e.* less pale) than can be matched directly, may be brought within this area by the addition of sufficient pigment

(such as white) to de-saturate the colour in question, till the resultant of the two is inside the area. The resultant and the added colours are then measured in terms of the instrument primaries, and the measure for the original colour obtained by difference. The shaded areas in the diagram represent the three coloured gelatin filters, through which the light from a "Fullolite" lamp passes. The prism CD rotates rapidly about the axis DE, so that as the end C passes each sectorial

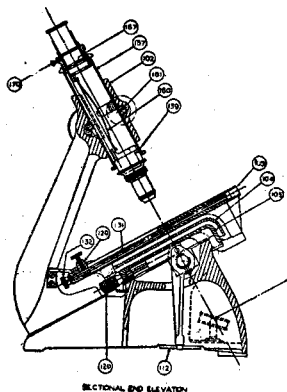


opening in turn, the light travels along the path DEFGH to the eye where the continued effect produces the sensation of a mixed colour. Each sectorial opening is fitted with a shutter to control the duration of the colour stimulus. The light from the colour to be matched (S) enters at I, and proceeds to the photometric prism (F), which acts as a matching field. The plane glass plate J is used in conjunction with the 45° prisms L and M to direct the source of light (or light of any desired colour) on to the field, where it is used for the purpose of de-saturation. The primary colours chosen are a red, blue, and green selected from a set of Wratten filters, and have wave-lengths of 0.63, 0.45, and 0.537 $\mu$ , respectively, saturated colours being chosen so as to make the colour field as comprehensive as possible. In practice, just enough of the third primary to make a match possible is added. Transparent objects are examined by light reflected from a white screen placed at S, opaque objects being themselves placed at S, and illuminated by light of any desired colour. The measurements may then be converted into a standard system of primaries. White light, similar to that of a black body at a temperature of 3000° to 5000° K, is obtained by the use of the following solutions in a double-cell filter :—(A) 2.30 grms. of copper sulphate and 230 c.c. of ammonia (density 0.9) in a litre of water ; (B) 13 grms. of copper sulphate and 12 grms. of cobalt sulphate in a litre of water. A piece of apparatus is described to enable colour measurements to be made by what is suggested as a standard method, *i.e.* with specimens normal to the direction of observation, illumination being confined to a narrow beam incident at 45°.

J. G.

**New Measuring Micrometer. J. H. Dowell.** (*Proc. Opt. Convention, 1926, Pt. 2, pp. 1-9.*)—The theory of micrometer construction is discussed from the point of view of the errors caused by slight changes in position of the mechanical or optical parts due to irregularities in the screw, carriage or slide. Errors due to

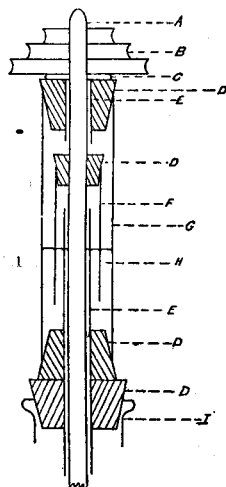
irregularities in the slide locating the carriage in a horizontal plane are avoided by fixing the microscope in the vertical plane of the screw axis just beyond the end of the micrometer screw. The corresponding vertical error is reduced by the use of geometric bearings for the carriage, the surfaces of which have errors which are small but all of the same order. These errors are measured by interference methods, and a tolerance of  $1/10,000$  mm. may be obtained with ease. The diagram shows a sectional end elevation of the new measuring micrometer, the outer tube of the microscope (137) of which is carried in the support (102), in which it may be firmly clamped by the draw-bolt (161). A casting (139) bearing at four points only and maintained on them by two springs (160), slides inside it and carries the objective and eyepiece. The rack works in a slot in the outer tube, and a large



range of adjustment is obtained by loosening the drawbolt (161), and adjusting the focussing mechanism to the range required. The milled head (120) enables the carriage to be moved by hand to the position of the starting point for measurements. The main carriage (103) bears at two and three points on the front and top surfaces respectively. Circular stops (129) in two slots on the table can be clamped on the rods (131), to which a fine motion can be imparted by the milled head (132); (112) is a correcting bar. The screw and slide are protected by a dust cover (104) placed between the main carriage (103) and the specimen table (105). The instrument measures up to 6 inches.

J. G.

**Modified Liquid Sealed Mechanical Stirrer.** G. S. Hiers. (*Ind. Eng. Chem.*, 1926, 18, 1203.)—In the usual type of stirrer three points of support are required, namely, at the flask I, at a point such as G, and at the usual bearing, which is inserted just below the pulley B. The modification shown in the figure uses a cork or rubber stopper which fits into the glass tube G, and which carries a glass or metal tube E, of the proper size to make a good bearing. Consequently, only two supports, at I and G, are required to ensure rigidity.



A—Stirrer shaft; B—Pulley  
C—Washer  
D—Cork or rubber stoppers  
E—Glass or metal tubes for bearings  
F, G—Tubing of proper size  
H—Mercury or other sealing liquid; I—Flask

W. P. S.

## References to Scientific Articles not Abstracted.

THE MECHANISM AND INCIDENCE OF INDUSTRIAL LEAD POISONING. *Lancet*, 1926, 211, 1132.

Inhalation of small quantities of insoluble lead compounds more dangerous than ingestion of very large quantities—Susceptibility of women—Damaging effects—Reproduction statistics.

THE ACTION OF LOBELINE. By F. R. CURTIS and S. WRIGHT. *Lancet*, 1926, 211, 1255.

Summary of chemistry of lobelia alkaloids—Physiological action of lobeline—Bibliography

ALLOTROPY. By Prof. A. SMITS. *Nature*, 1926, 118, 916.

Phase allotropy—Monotropy—Enantiotropy—Conglomerates of two modifications—Melting points—Boiling points—New theory of allotropy—Benzene as a mixture—Simple substances as mixtures with an inner equilibrium.

STUDENT PRECISION IN QUANTITATIVE ANALYSIS. By T. F. BUEHRER and O. E. SCHUPP, Jr. *J. Chem. Education*, 1926, 3, 1271 (November).

Factors influencing precision—Classification of factors—Factors for which the teacher is responsible—Factors involving method and apparatus—Factors involving skill, judgment and integrity—Conclusion.

---

## Reviews.

PHYSICAL AND CHEMICAL CONSTANTS. By G. W. C. KAYE and T. H. LABY. Pp. 161. Fifth Edition. London: Longmans, Green & Co., Ltd. 1926. Price 14s. net.

There are so many books of constants offered to the chemist that one naturally looks critically to see which gives the best value for money. A volume which has arrived at its fifth edition must be a good one, and "Kaye and Laby" has much to recommend it; it is a book which has proved its reliability and usefulness. The style and arrangement are clear and neat, and it is well printed on good paper. To the physical chemist it must be of great value as, indeed, it is a sort of miniature Landolt-Bornstein, but to the analyst, whose requirements are mainly chemical data with a few mathematical tables, it is open to the criticism that the price is too high in relation to the amount of data presented. There are other collections giving more data for a much less price, and one feels that a volume of only 161 pages ought not to cost 14s.—the same as in 1921.

The principal new features of this edition are tables of isotopes and of values for mechanical equivalent of heat. The chemist would like to see more details on common liquids (for example, the statement of refractive index of paraffin, 1.44, or olive oil at 1.46, does not tell us much), rather than have a list of nine determinations of "J."

H. E. Cox.

ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA: CHEMICAL, PHYSICAL AND TECHNOLOGICAL. Vol. V, part 2. Pp. lii + 805-1934. Paris: Gauthier-Villars et Cie; Cambridge: The University Press. 1926. Price £6 per volume.

The present volume completes Volume V of the annual tables and contains the numerical data determined and published during the years 1917-22 inclusive. It thus becomes evident that these tables are being brought up to date very rapidly. The vast amount of data contained in the volume is a testimony of the industry of scientific workers during the period covered, and of the care and thoroughness of those responsible for collecting and compiling the tables. Included in the work are data connected with ionisation potentials, X-ray spectra, radioactivity, cosmic physics, atomic weights, cryoscopic and ebullioscopic determinations, solubility, thermochemistry, chemical equilibria, velocity of reactions, photochemistry, photography, electrical conductance, electromotive force, colloidal chemistry, crystallography, biology, physiology, engineering and metallurgy.

The treatment of the data in this volume differs from that in the previous volumes in a few details, notably, photochemistry and photography are treated separately, and there is a modification in the treatment of the metallurgical data.

The amount of material contained in the volume is prodigious; the volume cannot fail to be of the greatest use to research workers and teachers, and it ought to be found in every research library, whether academic or technical. But despite the fact that much useful information on many technological subjects such as metals and alloys, lubricants, building materials and refractories, is included, it is very doubtful whether the book will prove useful to technologists generally, or will, indeed, be much used by them. The printing, indexing and general appearance of the book are satisfactory, save in one respect: in many places the diagrams show through the paper. It is to be hoped that this defect, small though it is, will not be found in future volumes.

J. F. SPENCER.

THEORETICAL ORGANIC CHEMISTRY (PART I). By FRANCIS ARNALL, Ph.D., M.Sc., F.I.C., and FRANCIS W. HODGES, M.Sc. Pp. xii + 372. London: J. & A. Churchill. 1926. Price 10s. 6d. net.

This book contains a first course of theoretical organic chemistry suitable for medical and pharmaceutical students, and for those taking the B.Sc. degree. The subject is developed in the approved manner—there are an historical introduction, a concise account of the methods available for the purification of organic compounds and a discussion of empirical and molecular formulae, followed by chapters on homologous series, the paraffins, their halogen derivatives, the alcohols, the ethers and so on through the carbohydrates and the ureides to the benzene compounds.

But although planned out in the usual way, no doubt to conform to the usual examination syllabus, the detailed treatment of the subject-matter is refreshingly

original. We have here no dictionary of the commoner organic compounds based on a framework of equations, but rather an eminently readable discussion of the underlying principles of theoretical organic chemistry, with considerable emphasis on the practical aspect of the science. There are incorporated in the text complete descriptions of no fewer than 115 illustrative experiments, so that stock phrases such as "Distilling A with soda-lime" or "Reducing B with sodium sulphide" will, to the student of this book, be something more than a mere form of words. Indeed, a sound course of practical organic chemistry could be based solely on the experimental directions given.

Subjects such as Isomerism, Tautomerism and Substitution in Aromatic Nuclei are treated in greater detail than is usual in a book of this type. Optical Activity has been particularly well done, the liberal use of diagrams adding to the clarity of the explanation.

Reference is made, where necessary, to the pharmaceutical and industrial applications of the substances described, and to the methods at present employed to manufacture them. In this connection it is interesting to find a brief account of "Synthol"; elementary text-books are not usually so up-to-date.

It is to be regretted that it is not customary to insert references to the literature in works of this kind. Such references have not only an educational value, but they also increase the interest of the student in his subject. Here, somewhat surprisingly, the authors have chosen to insert about three; why they should have stopped short at this number is not clear.

No higher praise can be given to this book than to say that it is entirely suitable for students who are studying privately and have not the advantage of a course of lectures. The printing and binding are up to the same standard of excellence.

T. S. WHEELER.

**TUNGSTEN: A TREATISE ON ITS METALLURGY PROPERTIES AND APPLICATIONS.**

By COLIN J. SMITHELLS, M.C., D.Sc. Pp. viii + 167. London: Chapman & Hall. 1926. Price 21s. net.

The author is a member of the Research Staff of the General Electrical Co., Ltd., and, as may be reasonably anticipated, the major portion of his book deals prominently with tungsten in the light of its use in electrical industry.

Viewed from this angle, the development of processes for filament production presents a record of scientific research in the face of apparently almost insurmountable difficulties, whilst the culminating success of Coolidge, who, in 1909, patented his method for the production of ductile tungsten by the application of heat-treatment and mechanical working, makes a fascinating appeal to the imagination, affording a notable example of world-wide benefit resulting from the patient industry of those workers to whom the problems have been allotted by choice or design.



In the earlier pages the preparation and purification of tungstic oxide is briefly outlined in general terms, with rather more detail in the case of the latter.

Methods for the reduction of the oxide are set out in two classes, the one product for use in the manufacture of alloys where a fairly wide latitude of quality is permissible, the other requiring to be free from impurities and in a suitable mechanical condition for the subsequent production of sheets and wire. Here, the technical processes now employed on a commercial scale are described, together with the methods for the determination of particle size, which latter governs largely the successful production of ductile tungsten, whilst the history of the metal from its initial state as powder to the final sheet or wire is clearly set out.

Two really excellent chapters on the metallography of tungsten present a clear and concise outline of the subject.

The control of grain size and recrystallisation under working conditions are fully considered; this matter has extreme significance, and, taken in conjunction with the many excellent photomicrographs, cannot fail to attract workers who have interest in the internal constitution of metals.

A short, but comprehensive, compilation of the properties of tungsten brings into line the most recent work, as is evidenced by the reference table at the end of the chapter; this feature, moreover, is common to the whole book.

One would have wished for a more generous treatment in the chapter on the determination of impurities in the metal, especially in view of their influence on its properties, and this chapter, together with the matter dealing with industrial applications, might have been extended with advantage.

As a whole, this treatise contains a wealth of detail set forth concisely and with organised method. The book can be recommended with confidence not only to those whose primary interest is in metals, but also to all to whom an account of the rapid progress due to the application of recent research and knowledge has its own peculiar appeal.

GEO. R. THOMPSON.

NATURAL AND SYNTHETIC RESINS. By T. HEDLEY BARRY, A. A. DRUMMOND, M.Sc., A.I.C., and R. S. MORRELL, Ph.D., F.I.C. Pp. vi + 196. London: Ernest Benn, Ltd. Price 21s.

In this work, Mr. Barry appears to have been responsible for the natural resins, and Messrs. Drummond and Morrell for the synthetic resins. The title of the work is a little misleading, as the preface informs us that the natural resins described have been confined to those used in varnishes. Hence, many substances dealt with by Dieterich in his well-known work and in Vol. IV of *Allen's Commercial Organic Analysis* are not even mentioned here.

It is quite impossible to deal adequately with this subject in the very small space which the authors have allotted to it. Only 112 pages, printed in large

type, are given to the natural (varnish) resins. Further, the length of the description of research work on colophony, with an inordinate number of graphic formulae, is out of proportion to the general scanty way in which the analytical aspect of resins has been treated.

Those resins which are included are, on the whole, accurately treated, but also, in general, on the same (or similar) lines as those to be found in the works above mentioned, except that the history, occurrence and commerce are given at somewhat greater length. Shellac, however, has not been treated so fully as it might have been. The American standards of examination are fully discussed, but there is no indication given that the London market has persistently refused to accept the United States standards, and that all shellac in this country is, for purposes of arbitrations, disputes, etc., tested by the Hübl method. Garnet lac is stated to contain up to 20 per cent. rosin. As a matter of fact, 10 per cent. is the trade standard, and from 9 to 12 per cent. is the amount found in actual deliveries. Moreover, pure garnet lac is a commercial article.

An analyst who wished to estimate the meaning of his determination of the acid value of shellac would, if he sought information here, be much puzzled. On page 20 the acid value of shellac (stick lac) is given as 34.7, and the insoluble matter (in alcohol) as 14.4 per cent. The true acid value of shellac is about 60. It is almost inconceivable that any analyst should determine and record the acid value of a sample of mixed shellac resin and the wood of the twigs on which the lac had been deposited (which mixture is, of course, stick lac), but if this be the case here, the acid value of such a mixture of 85 per cent. of shellac and 15 per cent. of insoluble matter would be about 50. On page 109, the correct figure, 61, is attributed to Hooper, whilst figures of 39, 53 and 59 are attributed to Rudling for stick, seed and button lac respectively. The author would have found a large amount of information as to the analysis of shellac if he had referred to papers published in the *Chemist and Druggist* (1901, 2, 689; 1902, 670; 1903, 1, 175, and 1905, 556).

On page 105 it is said that about 2.5 per cent. appears to be the minimum quantity of rosin that can be detected in shellac by the Liebermann-Storch test. In the hands of an experienced operator 0.25 per cent. can easily be detected. The figures given for rosin are misleading; the acid value is given as 145 to 185 and the saponification value 168 to 176. The fact that rosin never has an ester value over 12, and rarely over 6 to 8, cannot be gathered from the above figures. The iodine value of rosin is given as 116 to 257. The former figure is that of a Hübl, and the latter that of a Wijs determination, which should have been made clear.

On page 89 the author states that the acid value of dragon's blood is given by Dieterich in his "Analysis of Resins" as 137 to 139. As a matter of fact, the only acid value quoted by Dieterich is that found by Williams, namely, 11.2, and this figure is also that given in *Allen's Commercial Organic Analysis*. The figures 137 to 139 are those given by Dieterich as the *acetyl-acid* value—an entirely

different matter. Incidentally, every single figure given under dragon's blood is to be found in Dieterich's work, which contains a good deal more information as well.

One searches in vain under acaroid resin for the usual analytical values, whereas Rudling, so long ago as 1903, examined a number of samples and recorded iodine values, saponification values and acid values, all of which are exceptionally useful in the examination of this resin. All these values are to be found in other works. The only constant given for mastic is the acid value, whereas there are several records of ester and iodine values.

The book concludes with 68 pages on artificial or synthetic resins. This is a useful compilation for which patent specifications have been largely drawn upon, and, while interesting as a short summary of the subject, it does not give any material assistance to the analyst. It does not appear that the high price of this book is justified. It certainly carries the analyst no further than previously published books, and, generally, it does not carry him nearly so far.

ERNEST J. PARRY.

RECENT ADVANCES IN BIOCHEMISTRY. By JOHN PRYDE. Pp. vi + 348. London: J. & A. Churchill. 1926. Price 10s. 6d. net.

This book, which ranges in theme from subjects as chemically precise as carbohydrates and fats to others as elusive as "vitamins" and anti-gens, is to be heartily recommended as giving a clear and well-written review of the present trend of thought in biochemistry. The author has the knack of bringing order out of confusion and not only of giving past history and present view-point, but also of indicating the lines where the next advance may be anticipated. A particularly happy example of his success is the chapter on "Haemoglobin and Related Natural Pigments," where, under his skilful direction, the welter of terms that have become involved in this subject—haem, haemin, haematin, haemochromogen, haemoglobin, cytochrome, etc., etc.—all take on precise meanings, and there emerges an ordered chemistry of the relation of the respiratory pigment (in every known case a metallo-porphyrin derivative containing pyrrol rings) to the nitrogenous base (usually a protein) with which it must apparently be associated in order to attain maximum efficiency in the oxidative-reductive changes that form the basis of the life of the cell. The author gives in addition a very clear account of the analytical methods employed in detecting the existence of the various chemical individuals and the tests that decide whether respiratory pigments from various species and organs are identical or distinct. These methods are in nearly all cases spectroscopic, and the account of Hartridge's reversion spectroscope, not hitherto available except in the original papers, is a welcome inclusion.

Two other chapters, on nucleoproteins and on the chemical basis of immunity, also deal with bodies which consist of an association between a protein and some other group, and emphasise the important part which such complexes play in the dynamics of the living cell. The early stages in the development of biochemical

thought subdivided the materials of living matter into the three great groups of proteins, carbohydrates and fats, but it is becoming increasingly evident that the next stages will develop from the chemistry of border-line compounds.

Mr. Pryde deals in an illuminating manner with the recent work on carbohydrates, fats and vitamins, and compounds of phosphorus and sulphur. He includes a short chapter on protein catabolism and one on the physical chemistry of proteins. The latter hardly comes up to the standard of the rest of the work, while giving an adequate synopsis of Loeb's book, *Proteins and the Theory of and Colloidal Behaviour*, cannot be considered to give an unbiassed or even an adequate review of the present position of the theory of protein chemistry. No mention is made, for instance, of the important work of Pauli and his collaborators on the ionisation of proteins in solution, of that of Michaelis and von Szent-Gyorgyi on the shifting of the iso-electric point, nor of that of Wo. Ostwald on viscosity. It is also remarkable that no reference is made to Hardy's paper on the globulins, which appeared in the *Journal of Physiology* for 1905. In this pioneer paper there is a clear statement of the theory of salt formation between proteins and acids or bases, the role of the amino and the carboxylic groups in the two cases, and the nature of the iso-electric point as a point of equal ionisation of positive and negative ions and the influence of salts in shifting its position is shown experimentally. It seems, therefore, inaccurate to attribute "the view that proteins form compounds with acids and alkalis" to papers published fifteen years later.

The book is printed in the clear type characteristic of Messrs. Churchill's productions, and is practically free from misprints. It is a valuable addition to their "Recent Advances" series.

DOROTHY JORDAN LLOYD.

ANCIENT EGYPTIAN MATERIALS. By A. LUCAS, O.B.E., F.I.C. Pp. 242. London: Edward Arnold & Co. 1926. Price 7s. 6d.

Anyone who followed the accounts of the discovery of the Tomb of Tut-ankh-Amen will be familiar with the name—and portrait—of Mr. Lucas, who has been associated with Mr. Howard Carter in the work of restoring and preserving the wonderful collection of objects brought to light after so many centuries. Mr. Lucas has been resident for many years in Egypt, and was formerly Director of the Chemical Department. He is now Chemist of the Department of Antiquities, Cairo. Thus he has had unique experience and opportunities for study of the materials of which use was made in Ancient Egypt, and the results have been embodied in this book, which must be regarded as a companion volume to his recent work on *Antiques: Their Restoration and Preservation*. (Cf. ANALYST, 1925, 50, 102.)

Egyptologists will welcome the book as an authoritative account—from the view-point of the expert chemist—of the materials used by the Ancient Egyptians. This is a very fascinating field of research in applied chemistry, and presents problems of absorbing interest. In collecting and arranging the data at present available, Mr. Lucas has done a great service both to chemistry and to archaeology.

A specially valuable feature of the book is the very clear way in which fact is separated from speculation and hypothesis. In the past many mistakes have been made in the identification of ancient Egyptian materials, and these mistakes are reproduced from book to book, without enquiry or verification, until they come to be accepted without question. The student of Egyptology to-day is constantly engaged in sifting out the facts from the opinions of the earlier investigators, and for the beginner there are many pitfalls. Mr. Lucas is careful to point out these mistakes and how they originated, and where there is no certain knowledge, he wisely refrains from speculation.

The history of Egypt extends over a very long period. Because a material has been discovered to be in use at one time, it has been assumed to have been used throughout the whole history of the country. The plaster used was almost entirely gypsum plaster. The calcium carbonate and sand found on analysis are natural impurities in gypsum, which occurs plentifully in Egypt; they have been assumed to be due to an intentional admixture with lime, which in course of time has become converted into carbonate by natural processes, as is the case with lime mortar. In much of the large stone work, gypsum was used simply as a cushion to facilitate the positioning of the blocks. Lime plaster was not used before Roman times.

A great deal of light is thrown on much discussed problems such as the artificial hardening of copper and bronze for use as tools. Mr. Lucas makes it clear that there is no evidence that this was done, and that it is, in fact, an impossibility. Both arsenic and bismuth have been suggested as possible hardening agents, but both are natural impurities, and there is no evidence that they have been intentionally admixed. Copper may be hardened to a slight degree by cold-working, but it can never be made as hard as bronze. Bronze, on the other hand, can be treated so as to give a cutting edge, but not of the quality to be obtained from tool steel. We must look, therefore, in other directions for the solution of the problem. Mr. Lucas suggests that flint and abrasives, when used with unlimited time and the patience characteristic of the East, would have produced the results obtained. "In the early dynastic period, very hard material was successfully worked, and the introduction of bronze added no new triumphs in stone working."

Petrie has shown that a four-inch circular drill was used in the hollowing out of the sarcophagus in the King's Chamber of the Great Pyramid. This may have been accomplished by the use of an abrasive, such as emery, fed into grooves in the periphery of the tool. Herodotus assumes that iron tools were employed in the construction of the Great Pyramid, and much importance has been attached to a piece of iron found embedded in the masonry and now in the British Museum. As Mr. Lucas suggests, the analysis of this piece of iron might throw some light on its origin. Iron was certainly known in Ancient Egypt from a very early period, but was only occasionally made use of until about 850 B.C.

The author does not give us much information as to the composition of such materials as beeswax and resins. The physical and chemical constants are not

quoted. It is well known that Eastern beeswaxes have characteristic properties, and it would be interesting to know how Ancient Egyptian beeswax stands in regard to these.

Mr. Lucas's criticisms of Reutter's methods and results are fully justified. The smallness of the amounts taken for analysis must make one regard the results with suspicion. Nor can one attach much value to a probable identification which depends upon the smell of the substance or upon evidence based on a process of exclusion.

There are still many problems awaiting solution, such as, for example, the nature and use of dyes, the adhesive used in the manufacture of papyrus, tanning agents and paint vehicles. The author excludes white-of-egg from the possible paint vehicles on the ground that the domestic fowl was not introduced into Egypt until a late date. But surely, as Mr. Shrewsbury has pointed out (ANALYST, 1926, 51, 624), other kinds of eggs (*e.g.* those of crocodiles) were available in quantity.

Mr. Lucas adopts a scheme of chronology which has not yet met with general acceptance among Egyptologists, without a hint that there is any uncertainty in the matter of dating. But this is a very thorny subject.

The book is well arranged for easy reference. The nature or composition of the materials is given, and, where possible, the place of origin and the date when first used, and there is an excellent summary and index. It is a work which will be indispensable to the field worker as well as to the general student, and it is invaluable both as a collection of data and for the critical examination of the results. Mr. Lucas regards it as a preliminary venture, and it is to be hoped that he will continue his researches and publish further results in due course. The present volume leaves the reader thirsting for more.

R. W. SLOLEY.

EDIBLE OILS AND FATS: THEIR SUBSTITUTES AND ADULTERANTS. By G. D. ELSDON, B.Sc. Pp. xix + 521. London: Ernest Benn, Ltd. 1926. Price 45s. net.

It is evident from occasional statements in the text of this work that the author has felt the limitations laid upon him by the use of the word "edible" in its title. It is true that rosin and rosin oil have been used to adulterate linseed and other oils, and that a *hydnocarpus* fat has once been found in margarine, but croton oil is surely not edible because it is administered *per os* in quantity comparable with that of scheduled poisons, and it might even be questioned as to whether cheese falls into the category of edible fats.

The volume is, in fact, an excellent general treatise on the composition and analysis of fatty oils and of many substances containing them. It is of the greater value in that attention has been critically drawn to almost all recent publications on the subjects with which it deals, and the carefully edited references and bibliography which it contains are not the least of its valuable features. It has frequently

been stated that whilst books of this kind are excellent from an encyclopaedic point of view, particularly with regard to suggested analytical methods, they are lacking in that they contain neither sufficient criticism of the methods they describe nor any indication as to the most satisfactory process to employ in particular circumstances. The author has endeavoured to avoid this weakness by the introduction of a paragraph under the title "Method Recommended," which offers that authoritative advice which formerly has been conspicuous by its absence. Even more of these paragraphs would have been welcome than appear in the text.

The volume is well presented and contains few typographical errors in the general text, but misspellings are not infrequent in the botanical names for oleiferous plants. Possession of this book cannot fail to be a necessity to all chemists who are engaged in the large field of work which it covers.

JOHN ALLAN.

LAUNDRY CHEMISTRY. By A. HARVEY. Pp. 116. London: Crosby, Lockwood & Son. 1926. Price 4s. net.

The title of this little book is somewhat too ambitious, for it is quite elementary in its scope, and does no more than aim at giving those engaged in the laundry industry some idea of the chemical nature and properties of the materials which they handle. A short introduction is followed by chapters on acids, alkalis and salts, water and its softening, soaps, bleaching agents, starches, blues and blueing, and textile fibres, and the book concludes with a very useful section on the removal of stains. The author has the gift of making his subject clear in simple language, and his book makes interesting reading. It may however, have the unintended effect of making laundry men even more venturesome than they are in their chemical experiments on the garments of a trusting public, and it would have been well if the author had laid more stress on the dangers of over-bleaching or of too drastic attempts at the removal of stains.

EDITOR.

---

## Publications Received.

AGRICULTURAL RESEARCH IN 1925. ROYAL AGRICULTURAL SOCIETY OF ENGLAND. 1926. Price 2s. 6d.

YEAR-BOOK OF SCIENTIFIC AND LEARNED SOCIETIES. 1926. London: Charles Griffin & Co. Price 10s. 6d.

CHEMIKER ZEITUNG, 50TH ANNIVERSARY NUMBER (1876—1926).

MANUAL OF MEDICAL ASPECTS OF CHEMICAL WARFARE. THE WAR OFFICE. H.M. Stationery Office. Price 9d. net.