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THOMAS FAIRLEY, F.I.C.

In the death, on February 21, at the age of seventy-six, of Thomas Fairley, the Society of Public Analysts loses another of its few remaining founders, as well as one of the most respected of its past Presidents; and a large number of the individual members of the Society deplore the loss of a valued personal friend and of a loyal colleague in the profession of chemistry.

Besides being a sound chemist of the older school, Fairley was well read, and had a wide outlook on life, and was a pleasant companion in conversation that might wander far from professional topics. This makes it not a surprise to learn from letters of attestation of the early sixties placed in the writer's hands (through the kindness of Mrs. Fairley), that in early years spent in the Free Church Training College of Edinburgh—not his native city, for he was born in Glasgow—he earned the encomiums of his teachers for proficiency in Latin, Greek, English Literature, and Constitutional History, as well as in Mathematics, Geography, and Physical Science.

The taste for science, however, had manifested itself even earlier than this. Fairley unhappily lost both his parents when but four years old, and was brought up by an uncle who kept a school in Dumfries. Here—in his aunt's kitchen and somewhat to the discomfiture of that lady—he would dabble in chemical experiments with such limited apparatus as he could get, and this early acquired taste, developed at Glasgow, led later to his becoming first a student under and subsequently assistant to Lyon Playfair (afterwards Lord Playfair), of Edinburgh University. In this capacity he acquired considerable teaching as well as laboratory experience, and migrated to Leeds to become chemical teacher in the Leeds Grammar School, and lecturer in chemistry in the Leeds School of Medicine. At the same time he began to practise as a chemical consultant, and on the coming into operation of the Sale of Food and Drugs Act in 1873 he was appointed Public Analyst for Leeds and for the North Riding of Yorkshire. At a much later date, on the passing of the Fertilisers and Feeding-Stuffs Act, he also became official Agricultural Analyst, not only for the North but also for the West Riding, having been for many years interested in the agriculture of the county as consulting chemist to the Yorkshire Agricultural Society.

Down to the time of his death he was associated with many local educational matters, literary and scientific. He had acted both as Treasurer and as Chairman of the Yorkshire section of the Society of Chemical Industry, of which Society he also became Vice-President; also as President of the Leeds Naturalists' Field Association, and as Chairman of the Leeds Institute of Science, Art, and Literature, and while holding this office he was elected Chairman of the Council of the Association of Technical Institutions of Great Britain and Ireland in 1908.

He served a full term as examiner during the earlier days of the Institute of Chemistry, and became a Vice-President of that body, in whose welfare he always took an active and cordial interest; and his term of office as President of the Society of Public Analysts in 1903 and 1904 will be pleasantly fresh in the recollection of those of its members who were in the habit of attending the gatherings of the Society.

Fairley's earliest contribution to chemical literature was a paper published in volume xvii. of the *Journal of the Chemical Society* for 1864 on "The Action of Hydrogen on Organic Polycyanides." This paper incidentally records the first successful attempt at the synthesis of cyanoform, which the author prepared by heating together chloroform, potassium cyanide, and alcohol, at 100° C. under pressure. Fairley's experiment appears to have been successfully repeated seven years later by Pfankuch (see *J. Chem. Soc.*, 1871). Further contributions to that journal were: "Analysis of Water from the 'Old Crescent Well,' Harrogate" (1875); "A New Oxide and Acid of Uranium" (1876); and "Study of Hydrogen Dioxide and of Certain Peroxides, including Experiments to determine the Heat of Formation of the Oxygen Molecule" (1877).

To the Transactions of the British Association he contributed papers on: "Organic Cyanides" (1865 and 1868); "The Use of Platinum Black in the Preparation of Ethylene Diamine" (1868); "Preparation of Olefiant Gas" (1868); "Preparation of Cyanogen and Hydriodate of Cyanogen" (1870); "Use of Platinised Charcoal in the Hydrogenation of Cyanogen" (1870); and "The Distillation of Sulphuric Acid" (1870).

To the *Journal of the Society of Chemical Industry* he contributed: "Note on the Detection of Certain Adulterations in Dye-stuffs" (1886); "On the Estimation of Sulphur and Impurities in Coal Gas" (1886); "On the Various Forms of Filter-Pumps or Water-jet Aspirators" (1887); "On the Impurities of Coal Gas" (1892); "Note on the Durabilities of Platinum-Iridium Vessels in Laboratory Use" (1896); and "The Manufacture of Ammonium Nitrate by Double Decomposition" (1897).

Published in the ANALYST were the following papers: "Note on the Estimation of Chlorine in Water" (1893); "Arsenic Estimation Relating to Malt-kilns" (1901); "Notes on the History of Distilled Spirits, especially Whisky and Brandy" (1905); and "On the Phosphates in Certain Vinegars, and the Materials used in their Manufacture" (1909). The paper on the distillation of spirits, as very many readers of this journal may remember, was one recording the results of interesting antiquarian research into the early antecedents of an industry which at about that time was the subject of much legal contention and a monumental official investigation.

A paper on "The Water-Supplies of Yorkshire" was contributed in 1898 to the *Journal of the Federated Institute of Brewing.*

Various other papers and notes from Fairley's pen appeared at various times in the *Chemical News and Pharmaceutical Journal*, while not a few interesting fragmentary records of his practical experience are recorded in the reports in this and other journals of the discussions following on the papers of other authors. He was also one of the contributors on subjects connected with laboratory apparatus to Thorpe's "Dictionary of Applied Chemistry."

As gas examiner to the city of Leeds he became interested in questions relating to the manufacture and purification of coal gas, to which he devoted a good deal of practical attention.

His health and activity were well maintained until 1911, when he had an illness, from the effects of which he never completely recovered; but he was able, with the assistance of his old pupil and partner, Mr. B. A. Burrell, to continue to take, until quite recently, a responsible directive share in the conduct of his practice.

He is survived by Mrs. Fairley, but left no family. BERNARD DYER.

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

STUDIES IN STEAM DISTILLATION— PART VI.: THE POSSIBILITIES AND LIMITATIONS OF DUCLAUX'S METHOD FOR THE ESTIMATION OF HOMOLOGOUS ACIDS.

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

(*Read at the Meeting, May* 7, 1919.)

ALTHOUGH Duclaux's method for the estimation of homologous acids is over forty years old, it has not yet come into extensive use, partly because there is a doubt as to how far the results can be depended upon, partly because the calculations required after the experimental work is finished are too formidable for the average chemist lightly to undertake, and partly because the fundamental constants are not quite worked out with sufficient accuracy. Since Parts IV. and V. of this series (ANALYST, 1917, **42**, 125 and 133) were written, three papers have been published in America, which show forcibly the necessity of establishing the method in such a manner that it may now easily be available. Upson, Plum, and Schott (*J. Amer. Chem. Soc.*, 1917, **39**, 731) have adversely criticised Duclaux's method, chiefly because the results of any distillation of a mixture of fatty acids can be expressed not only in terms of the acids actually present, but within the limits of experimental error in terms of other acids. This contention has been answered by Lamb (*J. Amer. Chem. Soc.*, 1917, **39**, 746), and also by Gillespie and Walters (*J. Amer. Chem. Soc.*, 1917, **39**, 2027), and the last, in one of the most important papers on the subject, also give methods for calculating the results of analysis. There is one great defect about the paper of Gillespie and Walters, that they used acids which their results showed to be very impure, and they say that pure acids are not required to determine the constants, because the result of an analysis can be expressed in terms of an impure acid, which is a most pernicious doctrine, and one could equally well maintain that there is no reason for employing pure compounds to determine atomic weights, as the results of any analysis can be expressed in terms of incorrect atomic weight. Calculating the rate of distillation of their acids I find that the value is 0·441 for formic, varying from 0·437 to 0·443; 0·676 for acetic, varying from 0·670 to 0·683, indicating that these acids were probably pure, and the values are not far removed from my own for similar concentrations—viz., 0·419 for formic acid, and 0·684 for acetic. Their values for propionic showed a steady decrease from 1·250 to 1·142, indicating the presence of about 8 per cent. of acetic acid and 5·5 per cent. of butyric acid; and their butyric acid gave figures steadily falling from 1·88 to 1·475, showing approximately 10 per cent. of acetic acid. I believe that no one who has studied the distillation of aqueous solutions of the acids of the acetic series, has taken so much trouble to purify their acids, or so proved their purity, or worked with an apparatus and conditions so designed to eliminate error as I have done, and I therefore believe that my figures, though possibly not entirely correct, approximate more nearly to the truth than any hitherto published.

In Part I. of this series (ANALYST, 1908, **33**, 209), I discussed the theory of the subject, and by integrating the initial assumption, deduced formulæ expressing the laws of distillation. In Parts III. and IV. I gave the experimental data, and rates of distillation calculated therefrom, but it is seen that although the agreement is good all through, it is not perfect, and especially the first results have usually been rejected. This is partly due to the fact that the fundamental assumptions do not quite fit in with the experimental conditions. Thus, while the differential equation $\frac{dy}{dx} = a\frac{y}{x}$ is almost certainly true for the portions of the vapour, and liquid which touch at the surface, the ratio $\frac{y}{x}$ therein may differ slightly from the ratio $\frac{y}{x}$ in the whole of the solution; and similarly by the time that the vapour has passed up through the flask to the condenser, and has been condensed to liquid, which has dropped into the receiver, the ratio $\frac{dy}{dx}$ of the infinitesimal portion of vapour next the surface, is not necessarily quite the same as the ratio in the corresponding infinitesimal portion of the distillate. There is also another possible error introduced, because the molecular state of association is constantly varying to a slight extent.

For this reason I have considered that it will express my experimental results most accurately, and to be most useful to enable others to apply them to their own distillations if I give a series of tables, showing the quantity of each acid distilled, for each 10 per cent. by volume of the solution distilled, the table being divided according to the initial strength of acid (expressed in decimals of normal). I have included also a column $\frac{\Delta y}{\Delta x}$, which shows the percentage to be added for each 1 per cent. of volume distilled above the quantity stated (and subtracted if below), but this is not applicable for any large fraction (say up to 0·5 per cent. as a maximum). This is included, as it is far more easy to collect about the quantity required, and measure it accurately, than to collect an exact volume. The most convenient strength is about 0·04N, though with the higher acids a lower strength must be used, as the solubility is not high enough to ensure solubility in the first fractions if strong solutions are employed.

The tables given are results of the mean of a number of distillations of various strengths of acid, and include other determinations than those previously published.

Comparison with the distillations given in previous papers show that there are no large divergences. It has been found, however, that butyric acid shows more variation with concentration than had previously been assumed. The higher acids have only been distilled over a limited range for the reason named above, and it is not known whether they would also vary at higher concentration.

The apparatus and method of distillation have been given in Part III. (Analyst, 1908, **33**, 305), and this should be followed if the above tables are to be used (or, at least, some method of preventing condensation in the flask should be employed, such as that employed by Gillespie and Walters, *loc. cit.*). When the experiment has been performed, the results have to be calculated, and the tables may be used.

If two acids only are present, the equation for calculating the results is $a\mathrm{A} + b\mathrm{B} = \mathrm{R}$.

a = Fraction of acid (A) from table.	A = Fraction of acid (A) present.
b = ,, ,, ,, (B) ,, ,,	B = ,, ,, ,, (B) ,,
R = Fraction of acid actually distilled.	

This simplifies to $\mathrm{A} = \frac{\mathrm{R} - b}{a - b}$ and nine values are obtained of the ratio of the nine distillations $(\mathrm{B} = 1 - \mathrm{A})$. If three acids are present, the equation becomes $a\mathrm{A} + b\mathrm{B} + c\mathrm{C} = \mathrm{R}$, which simplifies to $\mathrm{A} + \mathrm{B}\frac{b - c}{a - c} = \frac{\mathrm{R} - c}{a - c}$, which gives nine simultaneous equations to be solved; and the problem is how to obtain mean values for A and B (and also for C, which is $1 - \mathrm{A} - \mathrm{B}$) with the least labour and greatest accuracy.

The methods are (1) that of the least squares, (2) the graphical method of Gillespie and Walters, (3) a method of solving simultaneous equations weighting according to magnitude. This last depends on the assumption that if $\frac{a}{b} = \frac{c}{d} = \frac{e}{f}$ very nearly, then $\frac{(a - c) + (a - e) + (c - e)}{(b - d) + (b - f) + (d - f)}$ is the best representation of their mean value. In practice $(a - c) + (c - e) = a - e$, and the formula which gives very good results is to take $2(a - i) + 3(b - h) + 2(c - g) + (d - f) + \frac{2}{3}\{(b - e) + (c - e) + (d - e)\}$ (a being the results for 10 c.c., b for 20 c.c., and so on).

The Relative Magnitude of Experimental Error.—In order that the method of least squares may be applicable to the calculation of "constants" in equation, it is essential that the "weight" attached to each observation should be the same; and the method of least squares becomes less and less reliable as the "weights" of the observations vary. The table below gives the relative error for each pair of acids named therein, calculated on the assumption that an error of 0·1 per cent. is made in the volume, and that *this is partly cumulative*, and calculated by expression:

$$\frac{0{\cdot}1 \times \sqrt{\text{Fraction distilled} \times 10} + 0{\cdot}1}{\text{Fraction of more volatile acid distilled} - \text{Fraction of less volatile}}$$

The errors calculated thus are relative, and are neither probable nor mean errors.

TABLE I.

Fraction Distilled.	Acetic-Formic.	P—A.	B—P.	V—B.	C—V.	B—A.	V—P.	C—B.	D—B.
10	7·2	3·9	3·6	3·5	42	1·9	1·9	3·2	2·5
20	4·1	2·6	2·6	2·3	19	1·3	1·2	2·1	1·5
30	3·2	2·1	2·2	2·0	19	1·1	1·0	2·0	1·3
40	2·7	1·9	2·1	1·9	22	1·0	1·0	1·8	1·2
50	2·5	1·8	2·0	2·0	26	0·9	1·0	1·8	1·4
60	2·4	1·8	2·2	2·4	43	0·9	1·1	2·3	1·8
70	2·4	1·9	2·4	2·4	50	1·0	1·4	3·2	2·7
80	2·6	2·2	3·1	5·8	?	1·2	2·0	5·7	5·1
90	3·5	3·1	5·2	20·0	?	1·9	3·9	20·0	19·0

From this table it is seen that when the acids are not higher in the table than butyric the ratio of the error of the first and last fractions to the mean of the other errors is 1·83 to 1; and with the higher acids the error of the first fraction is about of this order, and that of the last so great that it is practically negligible when it comes to weighting the determinations. It is evident that only half-weight can be attached to the first and last determinations with acids up to butyric, and with higher acids only half-weight to the first and eighth determinations, and none at all to the last. As it is only an assumption by mathematicians, in default of a knowledge of the true laws of error, that the value which gives a minimum value to the square of the errors of individual determinations is the best and the most exact value, as calculations by the method of least squares are very laborious, as the final value is obtained from an expression which is approximating to $\frac{0}{0}$, and therefore is liable to be greatly affected by any arithmetical error, as well as the fact shown above that some of the determinations have much less weight than others, and, moreover, the weight is very uncertain, the method of least squares is not to be recommended for calculating the results of a distillation. The graphic method has the advantage that it can be seen at once, if any unusual error is affecting any one determination as this one would be right off the line. Also, it would show that a wrong assumption as to the acids present has been made by the determinations not lying on a straight line. It suffers from the defect that the best straight line that can be drawn depends greatly on individual judgment, and especially there is a mental tendency to attach undue weight to the end determinations of the series which are the least reliable.

The third method has the advantage that it gives most weight to the most reliable determinations (see tables above), and labour of calculation is not excessive. As it is very little more trouble in using this method to plot up the data on a sheet of squared paper, it is recommended that the graphic method be employed as well.

Methods of Calculation.—The tables below give the difference between each pair of acids for each 10 c.c. distilled out of 100 c.c., together with difference factors for calculating small differences in volume. These may be used for calculating the values of $\frac{b-c}{a-c}$ and $\frac{R-c}{a-c}$, when the acids known or expected to be present have been chosen. To facilitate calculation still more, tables of the values of $\frac{b-c}{a-c}$ have also been calculated for mixtures of several series of three acids. The values of $\frac{b-c}{a-c}$ and $\frac{\mathrm{R}-c}{a-c}$ are then tabulated. They should be plotted out in squared paper, say 10 inches each way, and the straight line most nearly representing the points drawn. It will cut one axis at a point A unit from the origin and the tangent of the angle made (or the distance of the point where a line parallel drawn from the point 1 cuts the other axis) will equal B.

Next the values of $\frac{b-c}{a-c}$ and $\frac{\mathrm{R}-c}{a-c}$ for 90 c.c. are subtracted from those for 10 c.c. (1); those for 80 c.c. subtracted from those for 20 c.c. (2); those for 70 c.c. from those for 30 c.c. (3); those for 60 c.c. from those for 40 c.c. (4). Then the values for 50 c.c. are subtracted successively from those for 40, 30, and 20, and the sum of these three last called (5). The sum of $2(1)+3(2)+2(3)+(4)-\frac{2}{3}(5)$ for $\frac{\mathrm{R}-c}{a-c}$ divided by the similar sum for $\frac{a-c}{b-c}$ will give B. Next *nine* values of A are obtained from the equation $\mathrm{A}=\frac{\mathrm{R}-c}{a-c}-\mathrm{B}\frac{b-c}{a-c}$, and a probable value of A is best obtained by summing the nine values of $\frac{\mathrm{R}-c}{a-c}$ and $\mathrm{B}\frac{b-c}{a-c}$ and taking $\frac{1}{9}$ of the difference of the sums. The results by calculation should be close to those obtained graphically. A 10-inch slide rule is just good enough for the calculation, or four-figure logarithms may be used.

I fail to see any advantage in distilling 10 fractions of 10 c.c. each from 110 c.c., which is not a convenient quantity to measure accurately, and have consequently worked out all my tables for the distillation of 9 fractions of 10 c.c. each from 100 c.c.

TABLE II.

Formic Acid (A).

Strength as normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.							
10	0·43	3·95	4·0	4·0	4·05	4·05	4·1	4·1	4·15
20	0·47	8·3	8·4	8·5	8·60	8·65	8·75	8·90	9·05
30	0·51	13·4	13·5	13·6	13·75	13·8	13·95	14·05	14·15
40	0·56	18·65	18·85	19·05	19·25	19·3	19·6	19·65	19·75
50	0·62	24·6	24·8	25·0	25·3	25·4	25·8	25·9	25·95
60	0·71	31·05	31·25	31·55	32·0	32·2	32·8	32·9	33·05
70	0·85	39·15	39·35	39·65	40·1	40·3	40·9	41·0	41·15
80	1·06	48·55	48·75	49·05	49·5	49·7	50·3	50·4	50·55
90	1·60	61·9	62·1	62·4	62·85	63·05	63·65	63·75	63·9

Acetic Acid (B).

Strength as normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.							
10	0·71	6·45	6·55	6·65	6·75	6·8	7·0	7·0	7·05
20	0·74	13·55	13·8	13·9	14·0	14·1	14·3	14·3	14·35
30	0·77	20·9	21·25	21·35	21·5	21·6	21·85	21·9	21·95
40	0·80	28·85	29·2	29·4	29·55	29·65	29·8	29·85	29·9
50	0·85	37·2	37·55	37·65	37·8	37·9	38·15	38·2	38·25
60	0·91	46·15	46·5	46·6	46·75	46·85	47·1	47·15	47·2
70	1·00	55·65	56·0	56·1	56·25	56·35	56·6	56·65	56·7
80	1·16	66·25	66·6	66·7	66·85	66·95	67·2	67·25	67·3
90	1·41	78·75	79·1	79·2	79·35	79·45	79·7	79·75	79·8

Propionic Acid (C).

Strength as normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.							
10	1·22	12·35	12·4	12·4	12·4	12·45	12·45	12·5	12·5
20	1·18	23·9	24·1	24·2	24·4	24·5	24·7	24·7	24·7
30	1·14	35·7	35·8	35·9	36·05	36·1	36·2	36·2	36·2
40	1·10	46·8	46·9	47·0	47·1	47·2	47·4	47·5	47·6
50	1·05	57·2	57·4	57·6	57·7	57·75	57·9	57·95	58·0
60	1·00	67·3	67·5	67·7	67·9	68·0	68·2	68·25	68·3
70	0·93	77·1	77·2	77·3	77·4	77·45	77·6	77·65	77·7
80	0·84	85·6	85·8	86·0	86·2	86·3	86·45	86·5	86·5
90	0·71	93·8	93·8	93·8	93·85	93·85	94·0	94·0	94·05

Butyric Acid (D).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.				
10	1·80	19·9	20·15	20·4	20·5	20·55
20	1·60	36·2	36·6	37·0	37·2	37·3
30	1·40	51·1	51·5	51·9	52·1	52·2
40	1·20	63·75	64·15	64·55	64·75	64·9
50	1·00	74·5	74·9	75·3	75·5	75·6
60	0·80	83·3	83·7	84·1	84·3	84·4
70	0·60	90·35	90·75	91·1	91·3	91·4
80	0·40	95·25	95·65	95·9	96·1	96·2
90	0·20	98·85	98·95	99·05	99·1	99·15

Valeric Acid (E).

Strength as normal		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.
10	2·75	31·56
20	2·00	54·65
30	1·46	71·45
40	0·98	83·45
50	0·62	91·0
60	0·35	95·75
70	0·17	98·3
80	0·06	99·6
90	0·01	99·95

Caproic Acid (F).

Strength as normal		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.
10	2·79	32·55
20	2·03	56·85
30	1·41	73·45
40	0·93	85·00
50	0·57	92·05
60	0·31	96·35
70	0·14	98·65
80	0·05	99·7
90	—	99·95

Di-Ethyl-Acetic Acid (G).

Strength as normal		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Per Cent. Acid Distilled.
10	3·20	36·05
20	2·06	63·5
30	1·25	80·5
40	0·70	90·85
50	0·35	96·0
60	0·15	98·55
70	0·05	99·7
80	0·01	99·9
90	—	100·0

TABLE III.—DIFFERENCE TABLES.

Acetic Acid—Formic Acid (A).

Strength as normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.							
10	0·28	2·50	2·55	2·65	2·7	2·75	2·9	2·9	2·9
20	0·27	5·25	5·4	5·45	5·4	5·45	5·55	5·4	5·3
30	0·26	7·5	7·75	7·75	7·75	7·8	7·9	7·85	7·8
40	0·24	10·2	10·35	10·35	10·3	10·35	10·2	10·2	10·15
50	0·23	12·6	12·75	12·65	12·5	12·5	12·35	12·3	12·3
60	0·20	15·1	15·25	15·05	14·75	14·65	14·3	14·25	14·15
70	0·15	16·5	16·65	16·45	16·15	16·05	15·7	15·65	15·55
80	0·10	17·7	17·85	17·65	17·35	17·25	16·9	16·85	16·75
90	−0·19	16·85	17·0	16·8	16·5	16·4	16·05	16·0	15·9

Propionic Acid—Formic Acid (B).

Strength as normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.							
10	0·79	8·4	8·4	8·4	8·35	8·4	8·35	8·4	8·35
20	0·71	15·6	15·7	15·7	15·8	15·85	15·95	15·8	15·65
30	0·63	22·3	22·3	22·3	22·3	22·3	22·25	22·15	22·05
40	0·54	28·15	28·05	27·95	27·85	27·9	27·8	27·85	27·85
50	0·43	32·6	32·6	32·6	32·4	32·35	32·1	32·05	32·05
60	0·29	36·25	36·25	36·15	35·9	35·8	35·4	35·35	35·25
70	0·08	37·95	37·85	37·65	37·3	37·15	36·7	36·65	36·55
80	−0·22	37·05	37·05	36·95	36·7	36·6	36·15	36·1	35·95
90	−0·89	31·9	31·7	31·4	31·0	30·8	30.35	30·25	30·15

Butyric Acid—Formic Acid (C).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·37	15·95	16·15	16·4	16·45	16·5
20	1·13	27·9	28·2	28·5	28·6	28·65
30	0·89	37·7	38·0	38·3	38·35	38·4
40	0·64	45·1	45·3	45·5	45·5	45·6
50	0·38	49·9	50·1	50·3	50·2	50·2
60	0·09	52·25	52·45	52·55	52·3	52·2
70	−0·25	51·2	51·4	51·45	51·2	51·1
80	−0·66	46·7	46·9	46·85	46·6	46·5
90	−1·40	36·95	36·85	36·65	36·25	36·1

Valeric Acid—Formic Acid (D).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·32	27·6	27·55	27·55	27·5	27·5
20	1·53	46·35	46·25	46·15	46·05	46·0
30	0·95	58·05	57·95	57·85	57·7	57·65
40	0·42	64·8	64·6	64·4	64·2	64·15
50	—	66·4	66·2	66·0	65·7	65·6
60	−0·36	64·7	64·5	64·2	63·75	63·55
70	−0·68	59·15	58·95	58·65	58·2	58·0
80	−1·00	51·05	50·85	50·55	50·1	49·9
90	−1·59	38·05	37·85	37·55	37·1	36·9

Caproic Acid—Formic Acid (E).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·36	28·6	28·55	28·55	28·5	28·5
20	1·56	48·55	48·45	48·35	48·25	48·2
30	0·90	60·05	59·95	59·85	59·7	59·65
40	0·37	66·35	66·15	65·95	65·75	65·7
50	−0·05	67·45	67·25	67·05	66·75	66·65
60	−0·40	65·3	65·0	64·8	64·35	64·15
70	−0·71	59·5	59·3	59·0	58·55	58·35
80	−1·01	51·15	50·95	50·65	50·2	50·0
90	−1·60	38·05	37·85	37·55	37·1	36·9

Di-Ethyl-Acetic—Formic (F).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·87	32·1	32·05	32·05	32·0	32·0
20	1·59	55·2	55·1	55·0	54·9	54·85
30	0·74	67·1	67·0	66·9	66·75	66·7
40	0·14	72·2	72·0	71·8	71·6	71·55
50	−0·27	71·4	71·2	71·0	70·7	70·6
60	−0·56	67·5	67·3	67·0	66·55	66·35
70	−0·80	60·55	60·35	60·05	59·6	59·4
80	−1·05	51·35	51·15	50·85	50·4	50·2
90	−1·60	38·1	37·9	37·6	37·15	36·95

Propionic Acid—Acetic Acid (G).

Strength as Normal ...		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·20
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.							
10	0·51	5·9	5·85	5·75	5·65	5·65	5·45	5·5	5·45
20	0·44	10·35	10·3	10·3	10·4	10·4	10·4	10·4	10·35
30	0·37	14·8	14·55	14·55	14·55	14·5	14·35	14·3	14·25
40	0·30	17·95	17·7	17·6	17·55	17·55	17·6	17·65	17·7
50	0·20	20·0	19·85	19·95	19·9	19·85	19·75	19·75	19·75
60	0·09	21·15	21·0	21·1	21·15	21·15	21·1	21·1	21·1
70	−0·07	21·45	21·2	21·2	21·15	21·1	21·0	21·0	21·0
80	−0·32	19·35	19·2	19·3	19·35	19·35	19·25	19·25	19·2
90	−0·70	15·05	14·7	14·6	14·5	14·4	14·3	14·25	14·25

Butyric Acid—Acetic Acid (H).

Strength as normal		0·01	0·02	0·03	0·04	0.05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·09	13·45	13·6	13·75	13·75	13·75
20	0·86	22·65	22·8	23·1	23·2	23·2
30	0·63	30·2	30·25	30·55	30·6	30·6
40	0·40	34·9	34·95	35·15	35·35	35·4
50	0·15	37·3	37·35	37·6	37·7	37·7
60	−0·11	37·15	37·2	37·5	37·55	37·55
70	−0·40	34·7	34·75	35·0	35·1	35·05
80	−0·76	29·0	29·05	29·2	29·25	29·25
90	−1·21	20·1	19·85	19·85	19·75	19·7

Valeric Acid—Acetic Acid (J).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·05	25·1	25·0	24·9	24·8	24·75
20	1·26	41·1	40·85	40·75	40·65	40·55
30	0·69	50·55	50·2	50·1	49·95	49·85
40	0·18	54·6	54·25	54·05	53·9	53·8
50	−0·23	53·8	53·55	53·45	53·2	53·1
60	−0·56	49·6	49·25	49·15	49·0	48·9
70	−0·83	42·65	42·3	42·2	42·05	41·95
80	−1·10	33·35	33·0	32·9	32·75	32·65
90	−1·40	21·2	20·85	20·75	20·6	20·5

Caproic Acid—Acetic Acid (K).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·08	26·1	26·0	25·9	25·8	25·75
20	1·29	43·3	43·05	42·95	42·85	42·75
30	0·64	52·55	52·2	52·1	51·95	51·85
40	0·13	56·15	55·8	55·6	55·45	55·35
50	−0·28	54·85	54·6	54·5	54·25	54·15
60	−0·60	50·2	49·85	49·75	49·6	49·5
70	−0·86	43·0	42·65	42·55	42·4	42·3
80	−1·11	33·45	33·1	33·0	32·85	32·75
90	−1.41	21·2	20·85	20·75	20·6	20·5

Di-Ethyl-Acetic Acid—Acetic Acid (L).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	2·49	29·6	29·5	29·4	29·3	29·25
20	1·32	49·95	49·7	49·6	49·5	49·4
30	0·48	59·6	59·25	59·15	59·0	58·9
40	−0·10	62·0	61·65	61·45	61·3	61·2
50	−0·50	58·8	58·45	58·35	58·2	58·1
60	−0·76	52·4	52·05	51·95	51·8	51·7
70	−0·95	44·05	43·7	43·6	43·45	43·35
80	−1·15	33·65	33·3	33·2	33·05	32·95
90	−1·41	21·25	20·9	20·8	20·65	20·55

Butyric Acid—Propionic Acid (M).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	0·58	7·55	7·75	8·0	8·1	8·1
20	0·42	12·3	12·5	12·8	12·8	12·8
30	0.26	15·4	15·7	16·0	16·05	16·1
40	0·10	16·95	17·25	17·55	17·65	17·7
50	−0·05	17·3	17·5	17·7	17·8	17·85
60	−0·20	16·0	16·2	16·4	16·4	16·4
70	−0·33	13·25	13·55	13·8	13·95	13·95
80	−0·44	9·65	9.85	9·9	9·9	9·9
90	−0·51	5·05	5·15	5·25	5·25	5·3

Valeric Acid—Propionic Acid (N).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·53	19·2	19·15	19·15	19·15	19·1
20	0·82	30·75	30·55	30·45	30·25	30·15
30	0·32	35·75	35·65	35·55	35·4	35·35
40	-0·12	36·65	36·55	36·45	36·35	36·25
50	-0·43	33·8	33·6	33·4	33·3	33·25
60	-0·65	28·45	28·25	28·05	27·85	27·75
70	-0·76	21·2	21·1	21·0	20·9	20·8
80	-0·78	14·0	13·8	13·6	13·4	13·3
90	-0·70	6·15	6·15	6·15	6·1	6·1

Caproic Acid—Propionic Acid (O).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·57	20·2	20·15	20·15	20·15	20·1
20	0·85	32·95	32·75	32·65	32·45	32·35
30	0·27	37·75	37·65	37·55	37·4	37·35
40	-0·17	38·2	38·1	38·0	37·9	37·8
50	-0·48	34·85	34·65	34·45	34·35	34·3
60	-0·69	29·05	28·85	28·65	28·45	28·35
70	-0·79	21·55	21·45	21·35	21·25	21·15
80	-0·79	14·1	13·9	13·7	13·5	13·4
90	-0·71	6·15	6·15	6·15	6·1	6·1

Di-Ethyl-Acetic Acid—Propionic Acid (P).

Strength as normal … … …		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·98	23·7	23·65	23·65	23·65	23·6
20	0·88	39·6	39·4	39·3	39·1	39·0
30	0·11	44·8	44·7	44·6	44·45	44·4
40	-0·40	44·05	43·95	43·85	43·75	43·65
50	-0·70	38·8	38·6	38·4	38·3	38·25
60	-0·85	31·25	31·05	30·85	30·65	30·55
70	-0·88	22·6	22·5	22·4	22·3	22·25
80	-0·83	14·3	14·1	13·9	13·7	13·6
90	-0·71	6·2	6·2	6·2	6·15	6·15

Valeric Acid—Butyric Acid (R).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	0·95	11·65	11·4	11·15	11·05	11·0
20	0·40	18·45	18·05	17·65	17·45	17·35
30	0·06	20·35	19·95	19·55	19·35	19·25
40	−0·22	19·7	19·3	18·9	18·7	18·55
50	−0·38	16·5	16·1	15·7	15·5	15·4
60	−0·45	12·45	12·05	11·65	11·45	11·35
70	−0·43	7·95	7·55	7·2	7·0	6·9
80	−0·36	4·35	3·95	3·7	3·5	3·4
90	−0·19	1·1	1·0	0·9	0·85	0·8

Caproic Acid—Butyric Acid (S).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	0·99	12·65	12·4	12·15	12·05	12·0
20	0·43	20·65	20·25	19·85	19·65	19·55
30	0·01	22·35	21·95	21·65	21·35	21·25
40	−0·17	21·25	20·85	20·45	20·25	20·1
50	−0·48	17·55	17·15	16·75	16·55	16·55
60	−0·49	13·05	12·65	12·25	12·05	11·95
70	−0·46	8·3	7·9	7·55	7·35	7·25
80	−0·35	4·45	4·05	3·8	3·6	3·5
90	−0·20	1·1	1·0	0·9	0·85	0·8

Di-Ethyl-Acetic Acid—Butyric Acid (T).

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of Per Cent. Acid Distilled.				
10	1·40	16·15	15·9	15·65	15·55	15·5
20	0·46	27·3	26·9	26·5	26·3	26·2
30	−0·15	29·4	29·0	28·6	28·4	28·3
40	−0·50	27·1	26·7	26·3	26·1	25·95
50	−0·65	21·5	21·1	20·7	20·5	20·4
60	−0·65	15·25	14·85	14·45	14·25	14·15
70	−0·55	9·35	8·95	8·6	8·4	8·3
80	−0·39	4·65	4·25	4·0	3·8	3·7
90	−0·20	1·15	1·05	0·95	0·9	0·85

Caproic Acid—Valeric Acid (U).

Strength as normal ...		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of per Cent. Acid Distilled.
10	0·04	1·0
20	0·03	2·2
30	$-$0·05	2·0
40	$-$0·05	1·55
50	$-$0·05	1·05
60	$-$0·04	0·6
70	$-$0·03	0·35
80	$-$0·01	0·1
90	$-$0·01	—

Di-Ethyl-Acetic Acid—Valeric Acid (V).

Strength as normal ...		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of per Cent. Acid Distilled.
10	0·45	4·5
20	0·06	8·85
30	$-$0·21	9·05
40	$-$0·28	7·4
50	$-$0·27	5·0
60	$-$0·20	2·8
70	$-$0·12	1·4
80	$-$0·05	0·3
90	$-$0·01	0·05

Di-Ethyl-Acetic Acid—Caproic Acid (W).

Strength as normal		0·01
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Difference of per Cent. Acid Distilled.
10	0·41	3·5
20	0·03	6·65
30	$-$0·16	7·05
40	$-$0·23	5·85
50	$-$0·22	3·95
60	$-$0·16	2·2
70	$-$0·09	1·05
80	$-$0·04	0·2
90	—	0·05

TABLE IV.—FRACTIONAL TABLES.

$$\frac{\textit{Acetic Acid—Formic Acid}}{\textit{Propionic Acid—Formic Acid}} \text{ (A).}$$

Strength as normal		0·01	0·02	0·03	0·04	0·05	0·10	0·15	0·10
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Fractional Values.							
10	+0·0031	0·2976	0·3035	0·3147	0·3235	0·3273	0·3473	0·3452	0·3473
20	+0·0018	0·3366	0·3440	0·3440	0·3418	0·3438	0·3481	0·3418	0·3387
30	+0·0018	0·3363	0·3475	0·3475	0·3475	0·3497	0·3550	0·3544	0·3538
40	+0·0013	0·3623	0·3689	0·3702	0·3698	0·3709	0·3669	0·3663	0·3644
50	+0·0018	0·3864	0·3911	0·3881	0·3859	0·3864	0·3848	0·3838	0·3838
60	+0·0022	0·4166	0·4207	0·4163	0·4109	0·4093	0·4039	0·4031	0·4015
70	+0·0031	0·4348	0·4398	0·4369	0·4330	0·4320	0·4278	0·4269	0·4252
80	+0·0054	0·4777	0·4817	0·4776	0·4728	0·4713	0·4676	0·4668	0·4659
90	+0·0089	0·5278	0·5362	0·5341	0·5322	0·5323	0·5289	0·5289	0·5273
Σ		−1·217	−1·196	−1·133	−1·089	−1·050	−0·959	−0·983	−0·985

$$\frac{\textit{Propionic Acid—Acetic Acid}}{\textit{Butyric Acid—Acetic Acid}} \text{ (B).}$$

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Fractional Values.				
10	+0·0042	0·4377	0·4302	0·4182	0·4109	0·4109
20	+0·0023	0·4568	0·4517	0·4459	0·4482	0·4482
30	+0·0015	0·4901	0·4810	0·4763	0·4756	0·4740
40	+0·0028	0·5144	0·5065	0·5007	0·4964	0·4957
50	+0·0031	0·5362	0·5315	0·5293	0·5279	0·5266
60	+0·0038	0·5693	0·5645	0·5627	0·5631	0·5631
70	+0·0065	0·6181	0·6101	0·6056	0·6026	0·6018
80	+0·0063	0·6673	0·6610	0·6610	0·6600	0·6627
90	+0·0103	0·7487	0·7404	0·7355	0·7341	0·7308
Σ		−1·663	−1·660	−1·700	−1·706	−1·715

$$\frac{\textit{Butyric Acid—Acetic Acid}}{\textit{Valeric Acid—Acetic Acid}}\ \text{(C)}.$$

Strength as normal		0·01	0 02	0·03	0·04	0 05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Fractional Values.				
10	−0·0005	0·5360	0·5441	0·5522	0·5544	0·5555
20	+0·0032	0·5512	0·5581	0·5669	0·5709	0·5722
30	+0·0040	0·5955	0·6045	0·6117	0·6127	0·6139
40	+0·0054	0·6392	0·6442	0·6503	0·6558	0·6580
50	+0·0059	0·6933	0·6974	0·7036	0·7086	0·7101
60	+0·0068	0·7491	0·7553	0·7630	0·7663	0·7679
70	+0·0069	0·8136	0·8215	0·8294	0·8349	0·8356
80	+0·0069	0·8698	0·8802	0·8876	0·8932	0·8943
90	+0·0068	0·9482	0·9519	0·9566	0·9588	0·9610
		−2·522	−2·517	−2·507	−2·521	−2·421

$$\frac{\textit{Butyric Acid—Acetic Acid}}{\textit{Di-Ethyl-Acetic-Acid—Acetic Acid}}\ \text{(D)}.$$

Strength as normal		0·01	0·02	0·03	0·04	0·05
Per Cent. Volume Distilled.	$\frac{\Delta y}{\Delta x}$.	Fractional Values.				
10	−0·0034	0·4543	0·4610	0·4677	0·4692	0·4701
20	+0·0047	0·4535	0·4587	0·4657	0·4687	0·4697
30	+0·0064	0·5069	0·5122	0·5181	0·5186	0·5195
40	+0 0075	0·5628	0·5672	0·5719	0·5766	0·5797
50	+0·0086	0·6343	0 6390	0·6443	0·6474	0·6488
60	+0·0087	0·7091	0·7147	0·7218	0·7249	0·7263
70	+0·0086	0·7875	0·7950	0·8028	0·8078	0·8086
80	+0·0081	0·8620	0·8724	0·8796	0·8851	0·8880
90	+0·0075	0·9461	0·9499	0·9543	0·9563	0·9585
Σ		−3·170	−3·186	−3·186	−3·201	−3·218

It is quite impracticable to calculate with any degree of accuracy the results of a distillation of four or more acids, but there are methods of approximation which aid in the solution of such a problem. First there is the fact that formic acid can be estimated by taking advantage of the fact that it is easily oxidised to CO_2, the most reliable method in the presence of higher acids being the reduction of mercuric to mercurous chloride; and consequently a simple calculation will eliminate the effect of formic acid, and, if the quantity is small, the accuracy of the distillation of the other acids is not appreciably affected. Next, advantage can be taken of the fact that valeric and higher acids are practically all distilled, when 90 per cent. of the liquid is distilled, and consequently the higher acids are eliminated in this fraction; and although this is the least reliable determination, its accuracy is sufficient, in the case of the lower acids, to give an approximation to the quantity present (see example, Analyst, 1917, **42**, 137). Similarly, if the last fraction shows that the least volatile acids are not present in any large quantity, they are practically eliminated in the first fraction. It is difficult, however, to lay down any exact rules for such approximation methods, but as a chemist gains experience in the method he will be able to see how far the inspection of the ends of the curves aids.

The examples worked out below will show the manner in which the tables can be used to facilitate the working out of results. The working is all put down, though, naturally, much would be done mentally in practice.

Mixture of 20 c.c. N acetic acid + 20 c.c. of N butyric acid made up to 100 c.c.

(*a*) Calculated as a mixture of acetic and butyric acids :

Per Cent. Volume Distilled.	R.	R − Acetic.*	Butyric − Acetic.†	$\frac{R-A}{B-A}$.
10·0	13·6	6·85	13·75	0·498
20·0	25·6	11·6	23·2	0·500
30·0	36·8	15·3	30·6	0·500
40·1	47·3	17·67	35·39	0·499
50·0	56·6	18·8	37·7	0·499
60·0	65·5	18·75	37·55	0·499
70·0	73·8	17·55	35·1	0·500
80·0	81·45	14·6	29·25	0·499
90·0	89·2	9·85	19·75	0·499

$$\text{Mean value of } \frac{\text{butyric}}{\text{total}} = 0{\cdot}499.$$

If calculated as a mixture of acetic, propionic, and butyric acids, the value of (1) is −0·001, (2) +0·001, (3) 0·000, (4) 0·000, (5) 0·002. It is evident that the value of $\dfrac{\Sigma\frac{R-A}{B-A}}{\Sigma\frac{P-A}{B-A}}$ will be practically nothing ($= \frac{0{\cdot}0023}{-1{\cdot}706} = -0{\cdot}001$). The mean value will be :

Butyric acid	0·500
Propionic acid	−0·001
Acetic acid	0·501

A distillation of the propionic acid was made, from which the pure acid was prepared (see Part IV., Analyst, 1917, **42**, 125). This was estimated to contain, from the results of distillation in fractions, 2 per cent. of acetic acid, and 2·6 per cent. of butyric acid. A solution of 0·0394 N was made, and 100 c.c. were distilled.

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* From Table II. (B). † From Table III. (H).

Per Cent. Volume Distilled.	R.	R − A.*	B − A.†	$\frac{R-A}{B-A}$.	$\frac{P-A}{B-A}$.‡
9·9	12·55	5·87	13·64	0·4303	0·4105
19·95	24·45	10·49	23·16	0·4530	0·4481
29·95	36·0	14·54	30·57	0·4756	0·4755
40·0	47·1	17·55	35·36	0·4963	0·4964
49·95	57·95	20·19	37·69	0·5356	0·5277
60·0	67·95	21·20	37·55	0·5636	0·5631
70·15	77·75	21·35	35·04	0·6091	0·6036
80·15	86·4	19·38	29·14	0·6851	0·6609
90·15	94·6	15·04	19·57	0·7086	0·7367

Calculation of $\Sigma\frac{R-A}{B-A}$ (See p. 259).

$$\begin{array}{ll}
(1) & =0{\cdot}4303-0{\cdot}7086=-0{\cdot}2783\times 2=-0{\cdot}557 \\
(2) & =0{\cdot}4530-0{\cdot}6651=-0{\cdot}2121\times 3=-0{\cdot}636 \\
(3) & =0{\cdot}4756-0{\cdot}6091=-0{\cdot}1335\times 2=-0{\cdot}267 \\
(4) & =0{\cdot}4963-0{\cdot}5636=-0{\cdot}0673\times 1=-0{\cdot}067 \\
(5) & \left.\begin{array}{l}=0{\cdot}4530-0{\cdot}5356=-0{\cdot}0826 \\ =0{\cdot}4756-0{\cdot}5356=-0{\cdot}0600 \\ =0{\cdot}4963-0{\cdot}5356=-0{\cdot}0393\end{array}\right\}\times\frac{2}{3}=-\frac{0{\cdot}121}{1{\cdot}648}
\end{array}$$

Similarly $\Sigma\frac{P-A}{B-A}$ (it can also be worked out from the sum and the $\frac{\Delta y}{\Delta x}$ column) is $-1{\cdot}717$.

$$\frac{1{\cdot}648}{1{\cdot}717}=0{\cdot}960.$$

The total of the nine values of $\frac{R-A}{B-A}=4{\cdot}9372$, and of the *nine* values of $\frac{P-A}{B-A}=4{\cdot}9195\times 0{\cdot}96=4{\cdot}7233$, leaving 0·214, which divided by $9=0{\cdot}024$.

The composition of the acid is, therefore:

Propionic acid	...	...	0·960 or 96·0 per cent.
Butyric acid	...	...	0·024 „ 2·4 „
Acetic acid	...	...	0·016 „ 1·6 „

A solution of this propionic acid of 0·2 N strength was made up and 100 c.c. were distilled; the first 10 c.c., and approximately the last 20 c.c., were each made up to 100 c.c. and distilled in fractions with the following results:

* From Table II. (B).   † From Table III. (H).   ‡ From Table IV. (B).

First 10 c.c. 0·025 N.		Last 20 c.c. nearly 0·03 N.	
Per Cent. Volume Distilled.	Per Cent. Acid Distilled.	Per Cent. Volume Distilled.	Per Cent. Acid Distilled.
10·15	12·7	10·05	12·05
20·15	25·05	20·0	23·6
30·15	36·4	30·0	34·75
40·15	47·8	40·0	45·9
50·2	58·5	50·05	56·35
60·25	68·4	60·15	66·45
70·35	77·8	70·25	75·95
80·2	86·55	80·25	85·1
90·4	94·2	90·4	93·2

Calculated as before, the composition of the first 10 c.c. was acetic acid, 1·2 per cent., butyric acid, 5·05 per cent.; while that of the last 20 c.c. was acetic acid, 5·5 per cent., and butyric acid, 0·0 per cent.

From the tables the quantities distilled for 0·2 N should be—

	First 10 c.c.	Last 20 c.c.
Acetic	7·05	32·6
Propionic	12·05	13·5
Butyric	20·6	3·6

Dividing the percentages found above by the calculated quantities distilled just given, and calculating as percentages the composition of the original acid is—

	From First 10 c.c.	From Last 20 c.c.
Acetic Acid	2·1	2·4
Butyric Acid	3·0	—

The proportion of butyric acid in the last 20 c.c. is so small that the value 0·0 found does not represent a material error. The values calculated are all within 1 per cent.

Per Cent. Volume Distilled.	C.c. $\frac{N}{10}$ Soda used.	Per Cent. Formic Acid Distilled.*	$\frac{\text{C.c. } \frac{N}{10} \times 100}{\text{Per Cent. Formic Distilled}}$
20·0	5·04	8·7	57·9
30·0	8·00	13·87	57·6
41·5	11·60	19·99	58·0
52·5	15·51	27·15	57·2
60·3	18·73	32·7	57·3
68·4	22·48	39·24	57·2
79·1	25·51	49·05	58·0

Duclaux's method may be applied in a variety of ways:

(1) To estimate a volatile acid in a substance from which it cannot very con-

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* From Table II. (A).

veniently be separated: As an instance I give the results of the estimation of formic acid in Elixir Formatum B.P.C. which contains 5 per cent. each of sodium and potassium formates.

I am indebted to Miss Edith M. Ison, B.Sc., and Mr. H. N. Booth for their aid in this analysis; 5 c.c. + 7 c.c. $\frac{N}{1}$ H_2SO_4 were diluted to 100 c.c. and distilled.

It is seen that the agreement between the seven figures for the value of the total acid is good, which incidentally proves that formic acid is present; the mean value was 5·36 per cent., while the figure deduced from the known composition was 5·42 per cent.

2. To prove the purity of an acid: agreement with the values in the tables will show if the acid is pure, and a very stringent test is to distil an aqueous solution in fractions, make up the end fractions each to 100 c.c., and distil them separately in fractions; if the two distillations agree no appreciable amount of impurity can exist.

3. To determine small quantities of any impurity: the impurity should be concentrated either—(i.) by fractional distillation—*e.g.*, glacial acetic acid may be fractionally distilled with a good still head, and the portion boiling above 118° C. examined by Duclaux's method. I have in this way concentrated a small amount of propionic acid to 20 per cent. (ii.) By partial neutralisation as in Part 5 (ANALYST, 1917, **42**, 134). (iii.) By fractional distillation of an aqueous solution concentrating a more volatile acid in the early portions (see Richmond and Miller, ANALYST, 1906, **31**, 324), or a less volatile acid in the last fraction (see also *ante*).

I estimate that when two acids only are present the determination of their amounts can be made to about 1 per cent., and if three acids are present the error should be well under 5 per cent. by a single estimation, an error reduced to about 1 per cent. if a fractionation is performed.

Though the calculations, even with the help of the tables given, are a little tedious, there is in my opinion no method so rapid and accurate for estimating the proportions of volatile acids as that of Duclaux.

The experiments were performed in the Analytical Laboratory of Messrs. Boot's Pure Drug Co., Ltd., to whom my thanks are due, and I have also to express my indebtedness to Miss Mary Davis, B.Sc., for aid in the calculations.

* * * * *

A RAPID METHOD FOR DETERMINING NICKEL AND COBALT IN ORES AND ALLOYS.—PART III.

BY W. R. SCHOELLER, PH.D., AND A. R. POWELL.

(Read at the Meeting, June 4, 1919.)

THE two earlier communications on this subject appeared in the ANALYST (1917, **42**, 189; *Erratum*, 388), and the *Journal of the Iron and Steel Institute* (1918, **97**, 441; ANALYST, 1918, **43**, 301). The present paper concludes the account of our investigation, in the course of which we carried out nearly 600 cobalt and nickel determinations.

Further work on the method elaborated by us confirmed its reliability in quantitatively separating cobalt and nickel from iron, zinc, chromium, etc.; we were, however, unable to prevent co-precipitation of pentaminemanganous iodide; hence the presence of manganese renders additional manipulation unavoidable (see Ore L). Cases may also occur (*e.g.*, Ore M) where the simultaneous presence of elements which separately cause no trouble necessitates the adoption of a more indirect procedure.

The following important modification has been found necessary in the case of cobalt ores and alloys containing little or no nickel to promote the complete precipitation of hexaminecobaltous iodide. In describing the assay of cobalt-steel, we had occasion to mention that cobalt was precipitated less readily from tartrate solutions than nickel, and we counteracted this tendency by reducing the amount of tartaric acid after eliminating the bulk of the trivalent metals. We have since found that the addition of solid potassium iodide instead of a saturated solution of the salt to the ammoniacal tartrate liquor induces satisfactory precipitation of the cobalt (see Alloy Q).

A brief description of the further application of the iodide process to certain ores and alloys will now be given. As before, Mr. C. E. Barrs kindly undertook to check some of our results by electrolytic determinations.

L. Manganese Ore.

The material used was Wad containing 0·67 per cent. of cobalt. It was dissolved in hydrochloric acid; the solution was evaporated almost to dryness with nitric acid, and treated with tartaric acid, ammonia, and potassium iodide. An abundant white precipitate, containing all the cobalt and the bulk of the manganese, was produced. One of our unsuccessful attempts at preventing co-precipitation of manganese was based upon its conversion into manganic tartrate by the cautious addition of hydrogen peroxide to the ammoniacal tartrate solution before adding potassium iodide. But apart from the danger of also oxidising part of the cobalt, it was found that manganic tartrate was too unstable in presence of iodide to render a separation possible, as the solution always began to deposit crystals of pentaminemanganous iodide after a few minutes.

Other efforts to prevent the formation of the insoluble manganese compound having failed, recourse had to be had to a subsequent separation of manganese and cobalt. It may be useful at this point briefly to consider the available methods. All those in which either metal is brought to a higher state of oxidation are ineffective: thus manganese carries down cobalt when a solution of the two metals is treated with ammonia and bromine; cobalt interferes in Volhard's process, as does manganese in Winkler's cobalt titration. Neither the nitric acid-potassium chlorate mixture nor the persulphate precipitation of manganese fail to remove cobalt entirely. Small amounts of manganese may, however, be estimated colorimetrically in presence of cobalt, a fact which we have utilised in our process for assaying cobalt-steel, thus avoiding a separation. There remain the methods based on the different behaviour of sulphur compounds of the two metals. The process in general use consists in precipitating cobalt (nickel) sulphide in weak acetic acid solution, but it is not very suitable for rapid work as the filtrate from the cobalt sulphide must be concentrated and re-treated until no more black precipitate is obtained.

With a view to adopting a less tedious procedure we conducted a series of tests with the xanthate method which, while not new, does not appear to be employed to any extent. We found that the process is accurate and easy of execution. Thus, in Exp. 100:

Used, 0·1092 grm. Co.; added, 0·155 grm. Mn.; found, 0·1086 grm. Co.
Used, 0·1285 grm. Ni.; added, 0·155 grm. Mn.; found, 0·1282 grm. Ni.

In applying the process to the cobalt assay of manganese ore, the mixed manganese and cobalt iodide precipitate was dissolved in a slight excess of hydrochloric acid and the solution neutralised with ammonia in presence of cochineal. After addition of two drops of acetic acid, the cold solution was treated with excess of 5 per cent. solution of potassium xanthate whilst stirring vigorously to coagulate the precipitate, which was filtered off and washed with cold water. It was then boiled with nitric acid and a small quantity of potassium bromide till clear, and the cobalt precipitated and titrated as phosphate in the usual manner. Four consecutive assays (Exp. 101) gave 0·69, 0·67, 0·69, and 0·70 per cent.

M. Silver Concentrate (*Cobalt, Ont.*).

Composition (per cent.): Co, 4·80; Ni, 0·21; Mn, 0·08; Fe, 4·57; Ag, 20·94; As, 11·29; S, 1·48; Al_2O_3, 3·21; CaO, 6·81; MgO, 2·08; Insol., 39·17; difference (chiefly CO_2), 5·36.

This complex ore illustrates a case where the direct process (*cf.* Ore A) is not applicable. The following elements interfered by their combined action:

1. *Arsenic and Magnesium.*—These (as explained in Part I.) unite to magnesium ammonium arsenate in the ammoniacal tartrate liquor and contaminate the iodide precipitate, giving high cobalt results (*e.g.*, 6·42 and 5·61 per cent. in Exp. 130). We successfully overcame the interference of these two elements by expelling the arsenic in the following manner: the ore was dissolved in nitric acid and the latter driven off. The residue was boiled with hydrochloric acid and potassium iodide, whereby the arsenic acid was reduced and arsenious chloride volatilised. The assay was once

more taken to dryness with a fresh portion of hydrochloric acid to complete the removal of arsenic, after which the residue was again converted into nitrates. This method is more convenient than those previously suggested.

2. *Silver and Iron.*—Having secured a solution free from arsenic in the manner described, no further difficulty was anticipated in the cobalt assay by iodide, but on titrating the cobalt ammonium phosphate with $\frac{N}{5}$ acid there invariably remained a white amorphous precipitate which obscured the endpoint, though not badly. Thus, Exp. 135 gave 4·66 and 4·73 per cent. The white precipitate was found to be ferric phosphate, and the presence of iron at this stage was ultimately traced to occlusion or adsorption of iron, in spite of increased additions of tartaric acid, by the curdy white silver precipitate produced by potassium iodide in the ammoniacal tartrate solution; for, on first eliminating silver as chloride and submitting the concentrated filtrate to the usual iodide process, a clean precipitate of cobalt ammonium phosphate was obtained.

The amended iodide assay for complex ores, given in the Summary below (under (3)), is applicable to ores from the Cobalt district of Ontario.

N. Ferronickel.

Composition (per cent.): Ni, 44·90; Co, nil; Fe, 52·92; Mn, 1·25; Mo, 0·41. Insol., 0·14; total, 99·62.

0·5 grm. was dissolved in nitric acid, which was evaporated. Three grms. tartaric acid, 60 c.c. strong ammonia, and a saturated solution of 5 grms. potassium iodide were added. After twenty minutes, the precipitate was filtered and washed with ammoniacal iodide solution, then dissolved in dilute acid, and the nickel titrated with cyanide after addition of citrate solution (Sutton, 10th Ed., 269) as the manganese accompanied the nickel into the iodide precipitate. Found:

Exp. 143: 44·98 and 44·84 per cent. Nickel by electrolysis (C. E. Barrs): 44·88 per cent.

O. Chromenickel.

Trivalent metals (per cent.): Cr, 7·35; Fe, 1·20; Al, 0·75.

0·25 grm. was treated in the same manner as alloy N. Found:

Exp. 145: 89·81 and 89·90 per cent. Nickel by electrolysis (C. E. Barrs): 89·87 per cent.

P. Nickel Bullion (Copper Alloys).

The results were obtained in actual practice, when rapid assays of a considerable number of samples of high-grade and impure bullion were required. The figures represent eight consecutive assays taken at random. A quantity of 20-40 grms. of metal, according to coarseness, was dissolved in nitric acid and the solution made up to bulk. Aliquot portions equivalent to 0·5 and 0·1 grm. were subjected respectively to electrolysis by Mr. Barrs and to the iodide assay by the authors. The small quantity taken in the latter case was considered advisable in order to obtain a sharper endpoint in the direct cyanide titration. Some of the samples contained copper, a few up to 30 per cent.—*e.g.*, *j* and *k*; where present, this metal was removed as cuprous iodide after dissolving the mixed iodide precipitate in hydrochloric acid (*Cf.* Ores B and C). The cobalt, which was not estimated separately, amounted to 0·3-0·4 per cent. in all the samples. Considering the small quantity of metal taken for assay, the iodide figures are in fair agreement with those obtained by electrolysis, while for speed the iodide process again proved itself far superior.

Exp.	Electrolysis.	Iodide.	Exp.	Electrolysis.	Iodide.
146			146		
e	98·84	99·31	*i*	81·44	81·52
f	98·81	99·15	*j*	66·08	66·07
g	99·55	99·27	*k*	65·76	66·04
h	81·64	81·14	*l*	77·24	77·37

It was not deemed necessary to adduce further proof of the applicability of the iodide process to the assay of nickel-copper alloys. These would be treated as Ore C.

*Q. Chromecobalt.**

Ni, Mn : nil. Trivalent Metals (per cent.) : Fe, 2.4 ; Cr, 7 (approximately).

On account of the small amount of material (0·2-0·25 grm.) taken for the test analyses of this alloy containing over 90 per cent. of cobalt, the gravimetric estimation as pyrophosphate was adopted to obtain as close a check as possible on the accuracy of the iodide separation. The first assays in which the precipitation of the cobalt was done in the manner described for alloy O, were low and irregular, but when the slightly modified procedure given below (use of solid potassium iodide) was adopted, concordant results were obtained.

The alloy was dissolved in nitric acid, the solution made up to bulk, and an aliquot portion representing 0·2-0·3 grm. evaporated almost to dryness in a flask. Two grms. of solid tartaric acid were added, and dissolved in a minimum of water; the assay was treated with 20 c.c. of strong ammonia and 5 grms. of solid potassium iodide which was dissolved by rotating the liquid, after which another 30 c.c. of ammonia were added. The flask was stoppered and left to stand one hour with occasional shaking. The cobalt precipitate was filtered off and washed with ammoniacal iodide solution. The precipitation flask was placed under the funnel and the precipitate dissolved on the filter by stirring it up with a fine spray of hydrochloric acid (1 : 1) from a wash-bottle. A small quantity of sodium sulphite was introduced, and the acid liquor poured through the same filter into a beaker; the washing was done with hot water. The cobalt was precipitated as phosphate, the latter filtered off after half an hour, washed with cold water, dried, and ignited to pyrophosphate apart from the filter. The filtrate from the phosphate precipitate was treated with ammonium sulphide and the slight precipitate ignited to Co_3O_4.

Some of the observed deviations (±0·2 per cent.) may seem a trifle large, but as the work was done on little more than 0·25 grm., the absolute error was well below 0·001 grm. of metal.

Cobalt by electrolysis (C. E. Barrs) : 90·69 per cent. Took 0·2723 grm.

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* This alloy, as well as the chromenickel, was obtained from Messrs. Thermit, Ltd.

Exp.	$Co_2P_2O_7$ Found.	Co_3O_4 Found.	Cobalt, per Cent.	Error, per Cent.
158*a*	0·6084	0·0016	90·67	−0·02
158*b*	0·6072	0·0015	90·47	−0·22
158*c*	0·6080	0·0015	90·59	−0·10
159*a*	0·6105	0·0012	90·88	+0·19
159*b*	0·6081	0·0022	90·79	+0·10
159*c*	0·6087	0·0011	90·56	−0·13
			90·66 av.	

We are satisfied that the above procedure—namely, precipitation of cobalt ammonium phosphate and recovery of the last traces of cobalt in the filtrate by ammonium sulphide (or nitroso-β-naphthol) represents the most accurate form of cobalt estimation other than electrolysis. The precipitate produced by nitroso-β-naphthol is too bulky for any but small quantities. Cobalt ammonium phosphate is the most tractable cobalt precipitate known, and its very slight solubility can be corrected by testing the filtrate as described. Moreover, if nickel is present, the solubility is repressed, and the results liable to be high unless the precipitation is repeated. Cobalt ammonium phosphate may also be washed with 1 per cent. ammonium phosphate followed by dilute alcohol. (*Cf.* Grossmann, *Die Bestimmungsmethoden des Nickels und Kobalts*, Stuttgart, 1913.)

Additional Note on Cobalt-Steel.—With the experience gained in the assay of chromecobalt, we recommend the addition of solid potassium iodide instead of a saturated solution of the salt. In this manner what is described as "Method II." in the original paper need not be applied: this means a saving of labour in case a number of samples have to be assayed.

Iodide Recovery.—The method at first used consisted in precipitating the ammoniacal filtrates and washings with ferrous sulphate, filtering off the hexamine-ferrous iodide, heating it to drive off all the ammonia,.and boiling the residue with potassium carbonate. But while bivalent metals are precipitated quantitatively in ammoniacal solution by excess of iodide, the reverse does not hold good: the filtrate from the iron precipitate was still rich in iodine. We eventually adopted the following process: The ammoniacal liquor was evaporated to small bulk, and distilled with waste acid nitrate liquors in a capacious retort. The iodine so obtained, after washing and drying, was very pure and was used for volumetric work without sublimation. Many pounds of iodine were recovered in this manner.

Summary.

The following directions for the assay of ores summarise all the more important results of this investigation. For the assay of alloys, reference is invited to Parts II. and III. The assay of ores will be considered under four heads, according to the presence or absence of interfering elements.

1. *The ore is free from copper, manganese, lime, and magnesia ; presence of arsenic immaterial.* Dissolve in nitric or hydrochloric acid or both, but convert metals into nitrates ; take almost to dryness, avoiding separation of basic salts. Add tartaric acid (10 times the weight of trivalent metals) dissolved in a minimum of water. Add 50 c.c. of strong ammonia whilst cooling, and 3 to 5 grms. of solid potassium iodide according to the quantity of nickel or cobalt present. Allow to stand, stoppered, with occasional shaking, for fifteen minutes, or longer if cobalt predominates. Filter on loose paper, wash with ammoniacal iodide solution (4 per cent. of potassium iodide dissolved in 4 vol. strong ammonia : 1 vol. water). Dissolve precipitate in dilute hydrochloric acid, filter off gangue, precipitate cobalt as phosphate, titrate nickel in filtrate.

2. *The ore contains copper, otherwise the same as* 1. Proceed as above to the point where the iodide precipitate is dissolved in dilute hydrochloric acid. Decolorise the liquid with sulphurous acid, heat just to boiling, allow to cool, filter off insoluble gangue and cuprous iodide, apply phosphate separation.

3. *General procedure for complex ores free from manganese.* Dissolve in a suitable acid, precipitate heavy metals with hydrogen sulphide. To the filtrate add ammonium chloride and a slight excess of ammonia ; saturate with hydrogen sulphide, taking care to precipitate the whole of the nickel. Dissolve the precipitate in *aqua regia*, evaporate almost to dryness, etc., as under 1.

4. *The ore contains manganese.* (*a*) *Subordinate amounts.* Apply one of the preceding methods ; titrate cobalt ammonium phosphate with $\frac{N}{5}$ acid (not hydrochloric), or dissolve the weighed cobalt pyrophosphate in sulphuric acid. Determine the manganese colorimetrically with persulphate and silver nitrate in an aliquot portion of the cobalt solution, obtaining cobalt by difference.

(*b*) *Moderate to large amounts.* Dissolve the mixed iodide precipitate in dilute acid, and precipitate nickel and cobalt sulphides from an acetic solution. Or neutralise the acid solution and precipitate cobalt and nickel as xanthates. Either precipitate is dissolved in *aqua regia* and the two metals separated as before.

(*c*) With nickel ores free from cobalt, manganese does not interfere in the cyanide titration in the presence of citrate.

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AN IMPROVED METHOD FOR THE ESTIMATION OF NITRATES IN WATER BY MEANS OF THE PHENOLSULPHONIC ACID REACTION.

By ROBERT C. FREDERICK.

(*Read at the Meeting, June* 4, 1919.)

SPRENGEL'S method of estimating nitrates by means of the reaction with phenolsulphonic acid is probably that most frequently utilised in water analysis. The process is to evaporate 10 to 25 c.c. of the sample to dryness on the steam bath, and to treat the residue with 2 c.c. of phenolsulphonic acid; the whole is taken up with water, rendered alkaline with 20 c.c. of strong ammonia or potassium hydroxide solution, and made to a definite volume. The yellow colour of the nitro compound produced with nitrates is compared with that from a standard solution of potassium nitrate, and, by appropriate dilution and matching of the colours, the quantity of nitrogen as nitrates present in the sample is deduced. To prepare 1 litre of the phenolsulphonic acid reagent, 132 grms. of pure phenol is mixed with 60 c.c. of ammonia-free distilled water, and 815 c.c. of concentrated nitrogen-free sulphuric acid is added; the mixture is heated at 80 to 85° C. for six hours.

While it is well known that the presence of chlorides in the sample causes loss of nitrogen, it is perhaps not generally realised that the under-estimation is so great as to render the process inapplicable as a general method. The determination has been the subject of research by the writer, and a method which eliminates error has been evolved.

Effect of Chlorides on Sprengel's Method.

Solutions of potassium nitrate were prepared each containing 0·4 parts nitrogen as nitrate and varying amounts of sodium chloride as shown below. These were examined for nitrates by Sprengel's method, and the following results were obtained:

Cl per 100,000.	Nitrogen as Nitrates Found, per 100,000.	Percentage Error.
2·4	0·40	Nil.
9·2	0·35	−12·5
18·0	0·31	−22·5
30·0	0·27	−32·5
48·0	0·22	−45·0
60·0	0·18	−55·0
80·0	0·16	−60·0
100·0	0·16	−60·0

All natural waters contain chlorides, and the unreliability of the method is evident from the foregoing figures.

Effect of Addition of Phenolsulphonic Acid before Evaporation.

Some two years ago the writer tried the modification of adding the phenolsulphonic acid *before* evaporation and evaporating until all the water removable by steam heat was evaporated as shown by the residual acid liquid assuming a dark colour, a condition which may be conveniently termed here as "acid dryness." It was found that while the error due to chlorides was, to some extent, reduced, there was a persistent and irregular over-estimation. A series of sample solutions similar to the above, examined by this modification and compared with average "standards," gave the results undernoted:

Cl per 100,000.	Nitrogen as Nitrates Found, per 100,000.	Percentage Error.
2·4	0·42	+ 5·0
9·2	0·42	+ 5·0
18·0	0·42	+ 5·0
30·0	0·49	+22·5
48·0	0·55	+37·5
60·0	0·44	+10·0
80·0	0·42	+ 5·0
100·0	0·47	+17·5

Effect of Addition of a Diluted Phenolsulphonic and Sulphuric Acid Mixture.

The quantity of reagent employed in Sprengel's method is enormously in excess of that required to react with 25 c.c. of samples rarely containing more than 4·0 parts nitrogen as nitrates per 100,000. This was confirmed in practice by obtaining complete reaction with 0·08 c.c. of phenolsulphonic acid added to 25 c.c. of a solution of potassium nitrate of the above strength.

In view of this a phenolsulphonic acid solution was prepared by heating only 4 grms. of phenol with 25 c.c. of concentrated sulphuric acid and making to 1 litre. Two c.c. of this solution, added previous to evaporation, reacted completely with 25 c.c. of solutions of potassium nitrate containing nitrogen up to 4·0 parts per 100,000; but with natural waters reaction was incomplete, as the residue failed to remain liquid owing to the increased quantity of solid matter present. It was eventually found necessary, in order to make the solution effective for general use, to increase the sulphuric acid to 400 c.c. per litre; the amount of phenol remained unaltered.

Twenty-five c.c. of solutions of potassium nitrate, each containing 0·4 parts nitrogen as nitrates per 100,000, without chlorides, and with chlorides varying from 2·4 to 100 parts Cl per 100,000, were treated with 2 c.c. of the reagent before evaporation to "acid dryness," taken up with water, rendered alkaline with 3 c.c. of strong ammonia, and made to 100 c.c. The colours obtained in the final solutions varied with a maximum difference of only ± 5 per cent., and the solutions containing chlorides did not vary to a greater degree than those without, showing elimination of the error due to the presence of chlorides.

With a view to obtaining more thorough interaction between the nitrates and phenolsulphonic acid, a similar series was treated with the acid as above. In this series each water contained 0·4 parts nitrogen as nitrates per 100,000, four portions were without chlorides, and eight others contained 3·2, 10, 20, 30, 40, 60, 80, and 100 parts Cl per 100,000 respectively. The "acid dryness" residue was taken up with 5 to 10 c.c. of ammonia-free water, mixed, and again evaporated; this process of solution and evaporation to "acid dryness" was repeated. The residue was taken up with water and made alkaline as before. The colourations obtained were all equal, indicating that in this modification the nitrate value obtained was constant even in the presence of chlorides up to 100 parts of Cl per 100,000.

Further experiments were made to determine whether the colour intensity obtained in the final solution is proportionate to the amount of nitrate originally present. Samples of water were prepared containing 0·08, 0·2, 0·3, and 0·8 parts of nitrogen as nitrates associated with 40, 30, 20, and 40 parts of chlorine as chlorides per 100,000 respectively, and were examined by the final modification of the process. It was found that the intensity of the colours obtained with the prepared samples was in proportion to the amount of nitrate, showing that the colour varies directly with the nitrate present. In addition these results show that the method gives accurate determinations of nitrates in the presence of large and varying amounts of chlorine.

The accuracy of this process has been confirmed by examination of excessively hard waters containing large amounts of chlorides and (comparatively) high nitrates.

It has been noted when using the diluted phenolsulphonic acid and sulphuric acid mixture that the colour of the final solution is much more pure and brilliant than that obtained by the original method; this greatly facilitates accurate matching with the standards.

Detailed Process.

SOLUTIONS REQUIRED: *Standard Potassium Nitrate Solution.*—1·4434 grms. of pure KNO_3 per litre, 25 c.c. = 5·0 mgrms. N as nitrates; this solution is diluted 1 in 50, then 25 c.c. = 0·1 mgrm. N as nitrates.

Phenolsulphonic-Sulphuric Acid Mixture.—4 grms. of phenol (Calvert's No. 1 is very suitable) is mixed with 4 c.c. of ammonia-free distilled water and 100 c.c. of concentrated nitrogen-free sulphuric acid is added; the whole is heated at 80 to 85° C. for 6 hours, cooled, and made to 500 c.c. Three hundred c.c. of concentrated nitrogen-free sulphuric acid made to 500 c.c. with ammonia-free distilled water is added and mixed with the foregoing solution to give one litre of reagent.

METHOD.—Spherical-bottomed, 3½ inches diameter, porcelain basins are used each containing a small glass rod. To one basin 25 c.c. of the sample is added, and to the other 25 c.c. of the dilute standard potassium nitrate solution. Two c.c. of the phenolsulphonic-sulphuric acid mixture is added to each and thoroughly mixed by stirring. Both are evaporated on the steam bath until no more water is expelled ("acid dryness"), and the residual liquid assumes a dark colour. During the progress of the evaporation the liquid is occasionally stirred, and any dark spots on the side of the basin above the surface of the liquid are incorporated in the bulk of the residue by touching with the glass rod. The basins are then removed from the steam bath, and, by gently tilting them and directing the liquid with the rod, the residue is made to come in contact with all parts of the inside of the basin. All material on the sides of the basin is washed to the bottom with a very fine jet of ammonia-free distilled water; the 5 to 10 c.c. required is mixed with the bulk by stirring, and the whole is again evaporated to "acid dryness." The residue is once more taken up with water and evaporated to "acid dryness" as already described.

The final residues are taken up with water and poured into thin, colourless, measuring glasses, and the basins are washed out with small quantities of water to about 95 c.c.; 3 c.c. of strong ammonia (sp. gr., 0·880) is added and the whole made to 100 c.c. The contents of each glass are separately mixed by placing the palm of the hand tightly on the open end of the glass and inverting four or five times; to prevent loss of liquid, one edge of the lip of the glass is pressed tightly against the palm in withdrawing. The colour obtained in each glass is proportionate in intensity to the quantity of nitrate originally present.

A solution of potassium hydroxide may be used in place of ammonia, but is only satisfactory when prepared the same day. The colour obtained with a sample must always be compared with a standard prepared by the same process. In the few cases where the quantity of nitrogen as nitrates in a sample approximates or exceeds 4 parts per 100,000, the determination is repeated using only 10 c.c. of the sample; in the last 500 samples analysed by the writer, received from every kind of supply in all parts of the United Kingdom, this quantity has only been exceeded three times.

The advantages of this process may be summarised:

1. Nitrogen as nitrates, associated with chlorides up to 100 parts chlorine per 100,000, is accurately estimated.
2. The purity of the colours obtained in the final solutions makes matching easy.
3. The large saving of reagents is a consideration. Calculating on 2 c.c. of phenolsulphonic acid and 20 c.c. of ammonia used in the original process, there is a saving of 97 per cent. of phenol, 50 per cent. of sulphuric acid, and 85 per cent. of ammonia.

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MEXICAN INSECTS IN POULTRY FOOD: MEXICAN CANTHARIDES, *NOTONECTA*, *CORIXA*, AND *BEROSUS*.

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(*Read at the Meeting, June* 4, 1919.)

There are several poultry foods now sold in large quantities which are stated to contain insects, either whole or powdered. Such a food came into my hands recently for analysis, and a search for definite information upon the subject revealed the meagreness and unsuitability of the facts available. This has led me to pursue the inquiry further than was actually necessary for the needs of the occasion, and the results are of such interest that I have prepared the following account for communication to the Society.

The first sample examined was a poultry spice containing powdered insects, and, by sifting through a No. 20 sieve, the coarser particles were separated; these were sorted carefully under a magnifying-glass, and a number of heads, legs, and other insect fragments were picked out. I showed some of this débris to Mr. F. R. Rowley, the curator of the Exeter Museum, and he reported that the heads resembled those of water insects, and probably belonged to some species of *Corixa*. This information set me to work in the right direction, and I soon found some fragments of wing-cases undoubtedly belonging to a *Corixa*. The majority of the pieces of legs, however, did not agree with those of *Corixa*, and further investigation enabled me to identify them as belonging to the allied species *Notonecta*, or Water-boatman.

A further clue to their identity I obtained from Miall's description of the structure and habits of the water-bug, *Corixa*,[1] where he says "the eggs of two Mexican species (*C. mercenaria* and *C. femorata*) have long served as an article of food to the Mexicans." Sharp[2] makes the additional statement that "the insects themselves are used as food in both Mexico and Egypt." The commerce in these insects is referred to in the following terms by Howard:[3] "These Mexican species (*C. mercenaria* and *C. femorata*) are imported into England by the ton for game and song birds, poultry, and fish. Kirkaldy has computed that one ton contains 25,000,000 of these insects."

These writers make no reference to the admixture of *Notonecta* with *Corixa*, or to the occurrence of *Notonecta* in commerce at all. I found, however, in the "Year-Book of Pharmacy" for 1907 an abstract of a note by Hartwich,[4] who stated that a specimen of so-called Mexican cantharides, which he had examined, consisted mainly of insects of the genus *Notonecta*, closely allied to the common Water-boatman. This statement establishes the fact that dried insects of the Water-boatman type also come upon the market as an article of commerce. In response to my request, Dr. R. Eder, Director of the Pharmaceutical Institution of the Polytechnicum at Zurich, kindly sent me a reprint of the note by the late Professor Hartwich, and also a small specimen of the article which he had examined. In this material Hartwich identified *Notonectæ*, small bivalve shell-fish related to *Limnadia*, and in smaller amounts the larvæ of *Ephemerids* and *Stratiomys*. In addition to these creatures, I have found also some *Corixæ*, insects which appear to have escaped his notice.

Mr. C. J. Gahan, of the Entomological Department of the British Museum (Natural History) at South Kensington, showed me two samples of dried insects of commerce, one sent from Mexico in 1899, and consisting mainly of *Corixæ*, which were stated by the sender to be used as food for cage-birds and a second one labelled "Sample of dried flies used by naturalists for bird and fish feeding," sent to the museum for identification by a firm of dealers in London. The second specimen consisted of Water-boatmen and *Corixæ* mixed, the particular Water-boatman present having been identified by the museum authorities as *Notonecta undulata* (Say).

These facts show that there exists a regular commerce in dried insects from Mexico, and that the chief genera present are *Corixa* and *Notonecta* in varying proportions; sometimes, as in Mexican cantharides, *Notonectæ* predominate, and at other times *Corixæ* form the main component.

One of the samples of chicken food which I have examined contained these Mexican insects in an unbroken condition, and I was able to separate a considerable number from the food. Of these I sent some selected specimens to Mr. W. L. Distant, who kindly examined them, and compared them with specimens at the British Museum (Natural History). Mr. Distant found that the following species of *Corixa* and *Notonecta* were present: *N. undulata* (Say), *C. edulis* (Champ.), *C. kollari* (Fieb.), *C. mercenaria* (Say), and another uncertain species of *Corixa*. In the same sample there was also a number of small water-beetles identified as *Berosus mexicanus* (Sharp).

The genera *Notonecta* and *Corixa* both belong to the order Rhynchota (or Hemiptera), and are fully described in the works of Saunders,[5] and Douglas and Scott.[6] Figures of the British species are given in both works, while Douglas and Scott give also detail drawings, at a small magnification, of the legs and other structures. Kirkaldy[7] has given a full description of *N. undulata* (Say), but I have been unable to find any published descriptions of the other insects. The Mexican species closely resemble their British relatives, so that they are readily identified, so far as the genus is concerned, by reference to the works mentioned above.

The water-beetle, *B. mexicanus* (Sharp), may also be recognised from the illustrations and descriptions of the nearly allied British species of *Berosus* given in works upon the British Coleoptera, such as those of the Rev. Canon Fowler,[8] and Spry and Shuckard,[9] which latter book has an excellent line drawing of a *Berosus* closely resembling the Mexican insect.

When the insects have been more or less powdered in the preparation of the food, it becomes more difficult to recognise them, and it is a good plan to sift the material through a No. 20 sieve and examine the residue on the sieve with a hand lens.

The *Notonectæ* are chiefly represented in the débris by portions of legs and abdomens. The heads are so large and brittle that they are generally much broken, and fragments, including the eyes or parts of them, are found in small numbers only. The fragile elytra have very much the colour of chaff, and cannot easily be found among the siftings. The most characteristic fragments are the femora of the middle legs, each of which has a prominent sharp tooth near the apex. Portions of the hind legs are easily recognised by the dense fringes of hairs with which the feet and tibiæ are clothed. Occasional claws from the feet may also be found.

The *Corixæ* are recognised by the presence of numerous heads, which, being smaller and flattened, are much less easily broken than those of the *Notonectæ*. In addition, pieces of the characteristic elytra, with their vermiculate markings, are conspicuous under the lens, and can be picked out and identified. Portions of the oared hind legs will be found in fairly large numbers.

Berosus mexicanus is most easily identified in a broken or powdered condition by the elytra and heads. The elytra shows ten longitudinal rows of oval marks, each with a central dark spot, and these give them a very characteristic appearance under the microscope. Occasional specimens of the bronze-green head united to the brown prothorax are also to be found.

Poultry eat all these insects with avidity, picking them out from their food as if they found them very palatable, from which it appears that "Mexican dried flies," or "Cantharides," as they are sometimes called, form an excellent addition as a relish to poultry foods. The name "Cantharides" might lead one to fancy that some vesicant principle may be present, but it has been shown by Hartwich[4] that they contain no such substance.

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[1] Miall, L. C., "Natural History of Aquatic Insects" (1912), p. 360.

[2] Sharp, D., "Insects," Part II., "Cambridge Natural History," p. 568.

[3] Howard, L. O., "The Insect Book" (1902), p. 274.

[4] Hartwich, C., "Mexikanische Canthariden," *Schweizerische Wochenschrift fur Chemie und Pharmazie*, Zurich, **45** (1907), p. 73. Also "Year Book of Pharmacy" (1907), p. 190.

[5] Saunders, E., "The Hemiptera-Heteroptera of the British Islands" (1892), p. 329.

[6] Douglas, J. W., and Scott, J., "The British Hemiptera-Heteroptera," Ray Society, 1865.

[7] Kirkaldy, G. W., "Revision of the Notonectidæ, Part I.," Trans. Entom. Soc. of London, 1897, p. 410.

[8] Fowler, Rev. Canon W. W., "The Coleoptera of the British Islands," 1887, Vol. I., p. 229 and Plate 33.

[9] Spry, W. S., and Shuckard, W. E., "British Coleoptera Delineated," 1843, Plate 39, Fig. 3.

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NOTES.

The Editor desires 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.

NOTE ON AN ABNORMAL SAMPLE OF CASTOR-OIL.

THE explanation of the abnormally low viscosity of a sample of castor-oil prepared in Egypt from seeds produced there has proved very difficult, and information is sought from chemists who may have had a similar experience. The peculiarity lies in the fact that, though the specific gravity was somewhat low and the acidity high, the other values usually determined were normal, except the viscosity, which was quite exceptionally low. The sample was stored for over a year, and the viscosity was again determined, and found not to have changed at all. When 10 grm. samples were heated for an hour on a water-bath in flat dishes of the same size, it was found that about ½ per cent. loss of weight occurred, the amount being somewhat greater with highly acid samples. This loss appeared to be due to the removal of water, even in absolutely clear samples. The loss in the abnormal sample was in no way exceptionally great.

In the following table are shown the values given by another Egyptian sample and by three English samples as well as by the abnormal Egyptian oil.

	Sp. Gr. at 15·5° C.	Time of Flow (Redwood) at 60·0° C.	Acidity in Grms. KOH per 100 Grms. Oil.	Iodine Value (Hübl).	Saponification Value.
		Secs.			
English ...	0·9638	340	0·152	88	—
,, ...	0·9639	331	0·281	86	183
,, ...	0·9642	334	0·151	89	—
Egyptian ...	0·9575	262	0·987	87	184
,, ...	0·9618	319	1·644	87	—

The acetyl value of the sample with viscosity abnormally low was found to be 149, which is quite an average figure according to Lewkowitsch. It is hard to see how the low viscosity is to be explained in view of the iodine and acetyl values. The clarification of the sample was good, but the colour was a red-brown.

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THE EFFECT OF A FILM OF OIL ON THE AERATION OF WATER.

Although various chemists have remarked that a film of oil does not prevent the access of oxygen to deoxygenated water, this fact does not appear to be generally known, possibly because references to the matter have only occurred casually in the course of papers on other subjects. The following direct experiments may, therefore, be of interest:

1. Two portions of water were well boiled in open beakers. While still hot, one was covered with 10 c.c. of "kerosene." After twenty-four hours cooling and exposure to the atmosphere, the dissolved oxygen in the water was estimated in each case (by Winkler's method), and found to be 0·87 parts per 100,000 in the uncovered water and 0·82 in the oiled sample.

2. Three portions of water were well boiled as before. One was transferred to a narrow-necked flask filled to the top, cooled rapidly, and tested for dissolved oxygen. The second was left uncovered, and the third covered with "kerosene" to a depth of ¼ inch; both were cooled for three hours and brought to the same temperature by means of a water-bath, and the dissolved oxygen was then estimated:

The first portion (cooled rapidly) contained no oxygen.
The second (uncovered) contained 0·51 parts per 100,000.
The third (oiled) contained 0·50 parts per 100,000.

3. To some water was added a few drops of sodium nitrite solution, some dilute sulphuric acid, and then potassium iodide and starch solution. The liquid was divided into two parts, one of which was covered with a layer of light lubricating oil. Thiosulphate solution was carefully added to each, with gentle rotation of the liquid, till the blue colour just disappeared. Owing to the nitric oxide present in solution, the resulting liquid was extremely sensitive to oxygen, the absorption of which could be readily followed by the blue tint gradually developing at the surface, and diffusing down through the liquid.

No difference was noticed between the uncovered water and that covered with oil.

Herbert F. Stephenson.

Port of London Authority.

A GRAVIMETRIC METHOD OF COMPARING VISCOSITIES OF VARNISHES, ETC.

The apparatus used consists in its simplest form of a microscopical slide, two 100-c.c. glass beakers, each covered with a watch-glass and one of which contains a small wad of paper.

The microscope slide selected is about 3 inches in length, exactly 1 inch wide, and about 0·02 inch thick, and a fine scratch is made across the slide 2 inches from its lower end.

The slide is placed in the small beaker and rests with its lower edge on the paper wad. The watch-glass is replaced and the whole weighed to 1 mgrm. The varnish sample is filled into the second beaker and brought to the standard temperature, and the slide held vertically is immersed up to the scratch in the varnish. It is held there for five seconds, and then slowly withdrawn, still being held vertically, and kept suspended just out of the surface of the varnish for sixty seconds. The edge of the slide is then drawn across the edge of the beaker and the slide replaced in the other beaker, covered, and reweighed.

The difference in weight multiplied by 100 gives a viscosity figure which has served me for comparative purposes.

The following are some of the results I have obtained on several synthetic resin varnishes:

No. 13	0·366	0·373.	Average 0·370.	Viscosity at 15·5° C.	37·0
No. 14	0·442	0·441.	,, 0·442.	,, ,,	44·2
No. 15	0·411	0·411.	,, 0·411.	,, ,,	41·1
No. 16	0·390	0·380.	,, 0·385.	,, ,,	38·5
No. 17	0·438	0·428.	,, 0·433.	,, ,,	43·3

Rape oil at 15·5° C. gave the following results:

0·055 ... 0·055. Average 0·055. Viscosity ... ... 5·5

The rape oil serves as a means of standardising the slide.

The average thickness of the used portion of the slide was 21·6 mils—*i.e.*, 0·0216 inch; the maximum and minimum thicknesses being 22·2 and 21·1 mils respectively.

The average width of the used portion of the slide was 0·993 inch, the maximum and minimum widths being 0·9945 inch and 0·9910 inch respectively.

The advantages of this method of comparing viscosities are numerous:

1. Only small quantities (100 c.c.) of sample are necessary.
2. A corresponding short time is required to warm or cool the sample to the standard temperature.
3. Very little time is expended in cleaning the apparatus, the slide being very quickly cleaned, and the wad of paper which prevents the beaker from becoming dirty is removed, and a clean one substituted for each determination.
4. Once the sample is at the correct temperature duplicate results can be obtained in about five minutes.
5. The apparatus is suitable for very viscous solutions. A varnish which gave me a viscosity figure of 164 would not flow out of the Engler viscometer.

H. C. Siegfried de Whalley.

Micanite and Insulators Co., Ltd.,
Blackhorse Lane, Walthamstow.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Atropine. H. B. Rasmussen. (*Ber. d. pharm. Ges.*, 1917, **29**, 193-200; *Chem. Zeit.*, 1919, **43** [*Ref.*] 93.)—The following modification of the method of Bertrand and Javillier (*Bull. Sci. Pharmacol.*, **17**, 315, 360) is recommended as giving exact results: Six grms. of belladonna extract are mixed with 5 c.c. of alcohol and 5 c.c. of 20 per cent. ammonia solution, and shaken with 60 grms. of ether. After standing for three to four hours the ethereal layer is separated, and 50 grms. thereof shaken with three successive portions of 25 c.c. of 1 per cent. hydrochloric acid. The united acid extracts are filtered and treated with a slight excess of 10 per cent. silicotungstic acid, and, after standing for 8 hours, the precipitate is collected, washed with 1 per cent. hydrochloric acid, dried, ignited, and weighed. The weight multiplied by 0.4067 gives the amount of atropine, and an addition of 0·0054 grm. is made for each 100 c.c. of the liquid from which the atropine was precipitated.

C. A. M.

Estimation of Butter Fat, Coconut Oil, and Palm-Kernel Oil, in Mixtures. S. H. Blichfeldt. (*J. Soc. Chem. Ind.*, 1919, **38**, 150-152 T.)—Since the method described by the author was published (ANALYST, 1910, **35**, 399) a large number of results obtained by the method have been collected. The method has also been modified slightly; 100 c.c. of sulphuric acid (12·5 grms. per litre) is now employed in place of the stronger acid to decompose the soap, and a correction of 0·4 c.c. is deducted from the amount of $\frac{N}{10}$ alkali solution required to neutralise the total volatile fatty acids. A few of the average results obtained are as follows: *Coconut Oil.*—Total volatile acids, 21·0: insoluble silver salts, 17·6; soluble silver salts, 3·5. *Palm-Kernel Oil.*—Total, 13·7: insoluble, 11·0; soluble, 2·7. *Butter-fat.*—Total, 29·6: insoluble, 5·0; soluble, 24·6. The melting-point on the insoluble volatile fatty acids is of value in differentiating coconut and palm-kernel oils; for coconut oil fatty acids the melting-point is between 8° and 12° C., whilst for palm-kernel oil fatty acids it lies between 21° and 24° C.

W. P.S.

Analyses of War-Time German and Belgian Beers. H. L. Hind and J. L. Baker. (*J. Inst. Brew.*, 1919, **25**, 205-207.)—The beers analysed were collected in German and Belgian breweries between December 11, 1918, and February, 1919. The German beers were brewed before the districts were occupied by the British, and the Bavière was brewed at Brussels during the German occupation. The standard strength of German lager at the time of the Allied occupation was 1008°; inclusive of a tax of 5½ marks, the price was 34·5 marks per hectolitre. Owing to the shortage of malt, the gravities of German beers were reduced from an average of 1048° in 1914 to 1006° in 1917. Dulcin was added to the dark lager in amounts from 1 to 10 grms. per hectolitre. In Belgium such substitutes as beans, millet seed, tapioca, and vetches were employed.

Beer.	Original Gravity.	Apparent Gravity.	Remarks.
Sünner, Cölne-Kalk.	1001·02	1000·96	"Ersatz" beer, containing 1 grm. of dulcin per hectolitre. Very sweet to palate.
Althoven Brewery, Düren.	1007·90	1002·60	A typical dark lager. Good flavour.
Sturm Brewery, Düren.	1006·12	1001·94	A light lager. Very thin to the palate.
Germania Brewery, Cölne-Mulheim.	1005·78	1001·92	A light lager. Good flavour.
Winter's Brewery, Cölne.	1003·05	1002·0	"Ersatz" beer. Made from malt, flavoured with hops and dulcin, and coloured with aniline dye to resemble Munich beer. Sickly, sweet flavour.
Balsam Brewery, Mulheim.	1007·25	1002·0	Pale lager. Flavour good, considering its low gravity.
Merlo Brewery, Uccle-les-Bruxelles.	1013·86	1004·32	Typical of the top-fermentation beer brewed in Belgium. Fermented in casks, and ready for delivery about five days after mashing. Fair flavour.
Weilmans-Ceuppens, Bruxelles.	1006·08	1003·44	Bavière. Brewed during German occupation, and with a proportion of malt substitutes. Very thin to palate, but not an unpleasant beverage.
Weilmans-Ceuppens, Bruxelles.	1013·40	1006·56	Bock. Typical of the low fermentation beers brewed in Belgium. Very thin.

H. F. E. H.

Oil of Fenugreek. H. E. Wunschendorff. (*J. Pharm. Chim.*, 1919, **19**, 397-398.)—The seeds of fenugreek contain about 7 per cent. of a yellow oil, possessing a characteristic unpleasant odour. It does not solidify in the elaidin test, and when exposed in a thin film on glass dries rapidly, forming a bright yellow skin which is insoluble in ether. The oil is readily soluble in ether and petroleum spirit, incompletely soluble in acetone, whilst absolute alcohol dissolves about 5 per cent. in the cold, and a large proportion on heating. A sample had the following analytical values: Sp. gr. at 15° C., 0·9471; $[N]_{D\ 22\cdot5^\circ\ C.}$, 1·4774; acidity, 3·20 per cent.; saponification value, 189·5; iodine value, 137·8; Hehner value, 93·80; volatile fatty acids, 1·50 per cent.; unsaponifiable matter, 0·90 per cent.; and phosphoric acid, 0·55 per cent. The oil contained 6·25 per cent. of a lecithin and 0·5 per cent. of a phytosterol melting at 135·5° C. and forming an acetate (m.-pt. 131° C.). The fatty acids consisted mainly of palmitic and linolic acid, with a smaller quantity of oleic and linolenic acids. C. A. M.

Estimation of Gluten. Marchadier and Goujon. (*J. Pharm. Chim.*, 1919, [vii.], **19**, 425-429.)—The method proposed depends on the solubility of gluten in acetic acid. One grm. of the flour is mixed in a tube with 10 c.c. of glacial acetic acid, and the mixture is submitted to centrifugal action until the supernatant liquid is clear; five minutes at 1,500 revs. per minute is usually sufficient. The liquid is decanted and the deposit treated once more with acetic acid. The united acetic acid solutions are evaporated in a weighed basin on the water-bath, the residue is dried at 100° C., and weighed. W. P. S.

Meat Extracts: Their Composition and Identification. J. A. Emery and R. R. Henley. (*J. Agric. Res.*, 1919, **17**, 1-17.)—Muscle tissue alone was originally used for the extraction of meat extracts, but in more recent years, owing to the utilisation of waste products, other edible portions of the carcase are employed, such as livers, spleens, hearts, bones to which more or less meat adhered, etc., and in the present paper an attempt has been made to afford assistance to the analyst in enabling him to establish the identity of an extract under examination.

Some twenty meat extracts were prepared, some in factories under strict supervision using the commercial methods, and others in the laboratory. In the analysis of these extracts the methods used were essentially those described by Street (Thirteenth Report on Food Products for 1908: "Meat Extracts and Meat Preparations," *Conn. Agr. Exp. Sta. Bien. Rpt.*, 1907-08, pp. 606-672; Bib., pp. 664-672). A 10 per cent. solution of solid extract or a 20 per cent. solution of liquid extract was in all cases employed. *Water* was estimated by mixing some of the material with asbestos and drying to constant weight in a vacuum of 30 inches at a temperature of 60° to 65° C. *Chlorine* was determined on the ash by Volhard's method. *Coagulable nitrogen* was estimated by subjecting to the Kjeldahl process that portion of the extract precipitated by the addition of 0·5 c.c. of 10 per cent. solution of acetic acid when added to the extract previously evaporated on the steam-bath to half-volume, the heating after the addition of the acid being continued for a further fifteen minutes. *Ammonia nitrogen* was determined by the magnesium oxide method, and the proteose nitrogen was precipitated by zinc sulphate. The total nitrogen of the extract less the sum of the coagulable, insoluble, and zinc-sulphate-filtrate nitrogen represents the nitrogen of the zinc sulphate precipitate. Tannic-acid-salt nitrogen was also determined in the usual manner, and the nitrogen of this precipitate was obtained by subtracting the sum of the tannic-acid-salt filtrate and the coagulable and insoluble nitrogen from the total nitrogen. "Meat-base" nitrogen was obtained by subtracting the sum of the coagulable, insoluble, ammonia, and tannic-acid-salt precipitate nitrogen from the total nitrogen. Nitrogen due to peptone-like bodies was found by deducting the proteose nitrogen obtained by precipitation with zinc sulphate from the total quantity of nitrogen precipitated by the tannic-acid-salt reagent. *Purines* ("Report on the Separation of Meat Proteids," *U.S. Dept. Agr. Bur. Chem. Bul.*, 1905, **90**, 126-130): Three grms. of the sample were dissolved in 500 c.c. of a 1 per cent. solution of sulphuric acid, and heated for four hours in an open dish on the steam-bath. (At the end of this time about 75 c.c. should remain.) It was then neutralised with caustic soda, with litmus-paper as an indicator, transferred to a beaker, and 15 c.c. of a 15 per cent. solution of sodium bisulphite and 15 to 20 c.c. of a 15 per cent. solution of copper sulphate solution were added. This was allowed to stand overnight, filtered, washed with dilute copper sulphate solution, and the precipitate then washed with hot water from the paper into the original beaker. The contents of the beaker were brought to the boiling-point and sodium sulphide added to precipitate all of the copper. It was then placed upon the steam-bath for several minutes, made acid with acetic acid, and allowed to settle thoroughly, after which the precipitate was filtered off, washed with hot water, 10 c.c. of 10 per cent. hydrochloric acid added to the filtrate washings, and the solution evaporated to dryness on the steam-bath. Ten c.c. more of the 10 per cent. hydrochloric acid were added, and digestion was continued until the bases in the residue were dissolved. It was then filtered, washed, the filtrate made alkaline with 25 c.c. of strong ammonia, 10 c.c. of a 3 per cent. ammoniacal silver nitrate solution added, allowed to stand overnight, filtered on the following morning, the residue on the paper washed until all traces of ammonia were removed, and its nitrogen content determined. *Creatinine:* The method of Folin as modified by Emmett and Grindley was used (ANALYST, 1907, **32**, 171; 1908, **33**, 51; 1911, **36**, 288). *Creatine:* To 5 c.c. of the extract in a 50 c.c. graduated flask, 10 c.c. of $\frac{N}{1}$ hydrochloric acid and 5 c.c. of water were added, and the solution heated in an autoclave at 135° C. for thirty minutes. It was then cooled, 10 c.c. of $\frac{N}{1}$ sodium hydroxide added, and the solution made to volume with water. An aliquot was taken, and creatinine determined as above, with 30 c.c. of 1·2 per cent. picric acid and 10 c.c. of a 10 per cent. solution of sodium hydroxide, as suggested by Emmett and Grindley, the result so obtained representing the total creatinine—creatinine due to creatine, and to preformed creatinine. The difference between the total creatinine and the preformed creatinine multiplied by 1·16 represents the creatine. In the following table are given the results of the analysis of some commercial extracts—that is to say, samples prepared on the works scale (not in the laboratory) expressed on a water-free basis:

The most striking variations are the figures representing total nitrogen, "meat-base" nitrogen, creatinine, and non-nitrogenous organic matter. It was found that the liver and spleen extracts prepared under commercial conditions contain about ten times as much total creatinine as the laboratory extracts, this being attributable to the creatinine of the roast-beef soak water, defibrinated blood, and blood water used in clarifying these extracts. However, even though these commercially prepared liver and spleen extracts are relatively high in creatinine, they are, nevertheless, much lower than any of the other extracts. The greatest quantity of creatinine found in

Commercial Extracts (Water-Free Basis).

	Ash.	Organic Matter.	Non-Nitrogenous Organic Matter.	Sodium Chloride (Chlorine × 1·65).	Phosphorus.			Nitrogen.													Creatinine.	Creatine.
															Meat Bases.							
					Total Phosphorus Pentoxide.	Inorganic Phosphorus Pentoxide.	Ratio of Inorganic to Total.	Total.	Insoluble.	Coagulable.	Ammonia.	Zinc-Sulphate Precipitate.	Tannic Salt Precipitate.	Peptone-like Bodies.	Total (by Difference).	Creatine.	Creatinine.	Purines.	Undetermined.			
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent	Per Cent.	Per Cent.	Per Cent.		Per Cent.	Per Cent.
Beef spleens	26·59	73·41	24·07	8·41	4·04	2·83	0·700	9·98	0·18	0·00	0·34	3·00	5·17	2·17	4·16	0·27	0·62	0·88	2·47		1·70	0·88
Hog spleens	28·58	71·42	25·23	7·83	6·42	4·57	0·711	9·38	0·00	0·07	0·36	2·49	4·92	2·43	3 91	0·22	0·54	0·99	2·14		1·50	0·73
Roast beef soak water ...	38·10	61·90	19·70	13·42	7·25	6·62	0·902	8·99	0·09	0·00	0·39	0·92	3·96	3·04	4·49	0·28	2·58	0·67	0·98		6·94	0·89
Hog livers	25·65	74·35	44·96	10·22	5·76	3·62	0·629	6·00	0·03	0·05	0·11	1·12	3·20	2·08	2·59	0·20	0·58	0·65	1·16		1·59	0·61
Bare beef bones	35·20	64·80	19·17	11·02	6·55	5·94	0·900	9·47	0·12	0·00	0·28	1·34	4·73	3·39	4·33	0·44	2·28	0·69	0·79		6·18	1·38
Regular bones	34·48	65·52	21·62	10·84	6·07	5·49	0·904	9·59	0·20	0·00	0·29	1·44	4·27	2·83	4·80	0·50	2·42	0·68	1·18		6·60	1·59
Beef livers	26·58	73·42	40·62	10·03	6·42	4·05	0·630	6·59	0·03	0·07	0·11	2·07	3·68	1·61	2·68	0·28	0·56	0·62	1·22		1·54	0·89
Pickle	30·92	69·08	29·30	10·54	1·76	1·56	0·914	7·60	—	0·02	0·30	0·86	2·64	1·78	4·35	0·08	1·28	0·42	2·57		3·48	0·28
Beef hearts	31·10	68·90	29·74	9·70	6·98	5·90	0·845	9·02	0·08	0·00	0·49	1·55	3·61	2·06	4·84	0·40	1·70	0·77	1·89		4·63	1·26
Chuck and plate	28·90	71·10	24·20	6·72	7·66	6·46	0·844	10·08	0·00	0·08	0·37	1·79	4·45	2·66	5·14	0·63	2·11	0·70	1·71		5·69	2·00
Corn beef cook liquor ...	28·65	71·35	28·21	10·59	2·25	1·71	0·760	9·23	0·10	0·07	0·60	1·59	3 79	2·20	4·63	0·73	1·48	0·70	2·01		4·02	1·16

any of the liver and spleen extracts is 2·58 per cent. and the highest total creatinine —total nitrogen ratio—0·37, while the smallest amount of creatinine in the other extracts (except the pickle extract) is 5·38 per cent. and the lowest ratio 0·46. From these results it appears that all extracts of fresh flesh, with the exception of extracts of liver and spleen, contain more than 5 per cent. of total creatinine. Liver extracts are low both in total nitrogen and "meat-base" nitrogen; have a low inorganic phosphorus to total phosphorus ratio, are very low in total creatinine, and, as a rule, are very high in non-nitrogenous organic matter. Spleen extracts are high in total nitrogen, low in "meat-base" nitrogen, very low in creatinine, and lower than other extracts, liver excepted, in the inorganic-phosphorus to total phosphorus ratio. Heart extracts are low in total nitrogen as compared with chuck and plate extracts, but much higher than liver. They contain considerable non-nitrogenous organic matter, being next to liver extracts in this respect. Heart extracts differ from liver and spleen extracts in total creatinine and in "meat-base" nitrogen, the latter comprising at least 50 per cent. of the total nitrogen in heart extracts. Pickle and cured-meat extracts are readily identified by the presence of nitrates, which are always present in such extracts. The quantity of total phosphorus present in such extracts is very small. In other respects cured-meat extracts are found to resemble true-meat extracts. Pickle extracts contain rather less creatinine than true-meat extracts. Chuck and plate extracts run high in total nitrogen, "meat-base" nitrogen, and total creatinine, and have a high inorganic phosphorus to total phosphorus ratio. A qualitative test for the identification of spleen extracts was suggested by Chapin, who observed that the addition of an excess of acetic acid to a spleen extract results in the formation of an abundant precipitate. This was confirmed by Hammarsten who states that spleens are characterised by a peculiar protein soluble in boiling water and precipitated by an excess of acetic acid. All the commercially prepared spleen extracts were, therefore, tested for acetic acid, and it was found that with spleen extracts alone, of all the meat extracts prepared, was a decided precipitate obtained. It is easily distinguishable from the slight dark precipitate yielded by liver extracts, being very bulky and yellowish-white in colour. With mixed extracts it was found that not until the mixture contained approximately 20 per cent. of spleen extract was a decided reaction obtained. An extract of bone marrow fails to give an acid precipitate. The Molisch test was employed to help in the identification of liver extracts which contain comparatively large amounts of carbohydrates. It was used as follows: 1 c.c. of a 10 per cent. solution of solid or of a 20 per cent. solution of fluid extract was placed in a graduated glass-stoppered cylinder of 25 c.c. capacity, 9 c.c. of concentrated sulphuric acid were allowed to flow gently down the sides of the cylinder, and 6 to 10 drops of a 20 per cent. alcoholic solution of α-naphthol were then added. The stopper was inserted, and the contents of the cylinder were thoroughly mixed. In the presence of carbohydrates a persistent and intense reddish-purple to deep violet colour developed immediately. Working on mixtures of known content in order to determine the delicacy of the reaction, it was found that the characteristic colour was recognisable in an extract containing 20 per cent. of liver extract; smaller quantities gave a purple colour, but not sufficiently distinct to be of value. In all cases where a positive reaction is obtained, and in which the other factors, such as creatinine, nitrogen, etc., indicate the absence of liver extract, the sample should be examined for starch and cane sugar. Apart from its value in indicating the presence of liver extract, the Molisch test is necessary in a routine examination for the rapid detection of carbohydrates which may have been added to meat extracts. In the analyses of some hundreds of extracts a true-meat extract has never yielded a positive reaction with this test, and whenever a positive reaction is obtained in an extract which can be shown to contain no liver extract, it is due to added carbohydrate. In such instances the test should be supplemented with a more complete examination to identify the carbohydrate thus indicated. Copper test: It was noted that the ash of liver extracts in every instance exhibited a more or less pronounced greenish colour not observed in the ash of any of the large number of other kinds of extracts examined, and it is concluded that a greenish tinted ash should always lead to the suspicion that liver extract is present. If, however, copper utensils have been used in the preparation of the material, its presence in limited amounts would probably be readily demonstrated by chemical methods. The following procedure is suggested in the identification of an extract: (1) Total solids; (2) ash; (3) sodium chloride; (4) total phosphoric pentoxide; (5) inorganic phosphoric pentoxide; (6) total nitrogen; (7) "meat-base" nitrogen; (8) preformed creatinine; (9) creatine; (10) Molisch test; (11) acetic-acid test; (12) test for starch and sugar if a positive Molisch test is given; (13) test for nitrates; (14) test of ash for copper. The quantities of insoluble, coagulable, and ammonia nitrogen are so small in all ordinary extracts that they are determined only in case they are indicated in extraordinary amounts. Should an extract show an unusually high nitrogen content, a study of the various forms of nitrogen present is essential. After an examination of an extract as suggested, its accurate classification as a true-meat extract, as a cured-meat extract, as a compound extract, or as an extract of liver or spleen is possible, and at the same time the addition of foreign material, such as sugar, starch, or salt will be established. (See ANALYST, 1915, **40**, 310-326.) H. F. E. H.

Estimation of Purine Bases in Foods. T. von Fellenberg. (*Mitt. Lebensm.-Untersuch. Hyg.*, 1918, **9**, 73; through *Chem. Zeit. Rep.*, 1919, **43**, 90.)—The author has estimated the purine bases in some 170 animal and vegetable substances, Kruger and Schittenhelm's method, with slight variation, being used for the purpose. In the case of meats and spinach, about one-half of the purine bases passed into solution when the sample was boiled with water; cauliflower yielded no water-soluble purine bases. Of animal substances, all internal organs had a high purine content; then followed fish, birds, muscular tissue, and blood. Sinew, bone, fat, milk, and eggs were almost free from purine. All vegetable substances containing alkaloids had a high purine content; then followed lettuce, spinach, cabbage, mushrooms, radish; potatoes contained but little purine. The small quantity of purine bases found in legumes and cereals was located in the aleurone layer and the germ. The smallest quantity of purine bases was found in the oil seeds. W. P. S.

Estimation of Salicylic Esters in Fatty Oils. P. Behrisch and F. Kurschner. (*Apoth. Zeit.*, 1918, **33**, 20; through *Chem. Zeit. Rep.*, 1919, **43**, 92.)—The method depends on the difference in solubility of the alkaline earth salts of salicylic acid and those of fatty acids. The substance is saponified with alcoholic potassium hydroxide solution, the mixture diluted with water, neutralised with hydrochloric acid, and the fatty acids precipitated with barium chloride. After filtration, an aliquot portion of the filtrate is acidified with hydrochloric acid, the salicylic acid extracted with ether, the ether evaporated from the extract, the residue obtained dissolved in alcohol and titrated with $\frac{N}{10}$ potassium hydroxide solution, using phenolphthaleïn as indicator. W. P. S.

Halphen's Ratio as Applied to Italian Wines. G. Halphen. (*Ann. Chim. anal. Appl.*, 1919, **1**, 185-186.)—In reply to the criticisms of Scurti and Rolando (ANALYST, 1918, **43**, 37) it is suggested that those chemists have not given to the ratio between the amounts of alcohol and acid the interpretation accepted in France. The only conclusion to be drawn is that when the ratio falls below that marked on the curve, the addition of water to the wine is indicated. The rule applies to 98 per cent. of French, Algerian, and Tunisian wines, and applied in this way would also be found of use in detecting the watering of Italian wines. C. A. M.

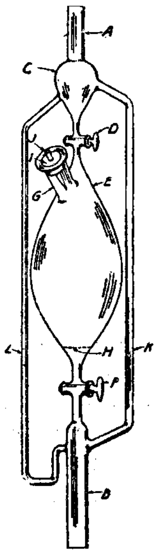
BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Methods of Testing Gas Masks and Absorbents. A. C. Fieldner, G. G. Oberfell, M. C. Teague, and J. N. Lawrence. (*J. Ind. and Eng. Chem.*, 1919, **11**, 519-540).—The development and manufacture of gas masks and absorbents depend to a large extent on properly designed tests which simulate the actual conditions under which the mask is to be used. In the present paper, the tests employed by U.S. Chemical Warfare Service are described in great detail and well illustrated. As most of the methods were completely worked out before collaboration with the British and French was established, there is much matter here which is now made public for the first time. G. C. J.

ORGANIC ANALYSIS.

Estimation of Small Amounts of Benzene in Ethyl Alcohol. F. W. Babington and A. Tingle. (*J. Ind. and Eng. Chem.*, 1919, **11**, 555-556.)—To 100 c.c. of the sample 200 c.c. of water are added, and the mixture distilled slowly (not faster than 1·5 c.c. per minute). About 20 c.c. of the distillate are collected in a 50 c.c. Eggertz tube or in a 50 c.c. burette, and if the appearance of the mixture after dilution suggests the presence of more than 0·75 per cent. of benzene, a further 10 c.c. are collected in a second tube or burette. To the distillate in each tube are added 15 c.c. of potassium dichromate solution ($\frac{1}{6}$ saturated) and 3 c.c. of concentrated hydrochloric acid, after which the tubes are closed with rubber stoppers and the contents mixed and allowed to stand until an olive-green colour develops (fifteen minutes). An accurately measured volume of petroleum ether (10 c.c.) is added, the contents once more shaken, and the volume of the upper layer read. This volume less 10 c.c. gives the percentage of benzene in the sample. If the sample contains from 0·8 to 1·6 per cent. of benzene, a measurable amount, but not more than 0·1 c.c., may be found in the second portion of the distillate. No experiments with higher concentrations are described, the method having been designed to determine whether samples of denatured spirit conformed to a regulation prescribing the addition of 0·5 per cent. of benzene. The maximum error of the method is 0·1 per cent. on the sample, whereas the method of Holde and Winterfeld (ANALYST, 1908, **33**, 242) is shown to be quite useless for the estimation of such small proportions of benzene as 0·5 per cent. G. C. J.

Organic Chemical Reagents, IV. Preparation of Alkyl Iodides. R. Adams and V. Voorhees. (*J. Amer. Chem. Soc.*, 1919, **41**, 789-798.)—Walker has recommended the use of a mixture of yellow and red phosphorus instead of red phosphorus alone for this purpose, and designed a suitable apparatus which permitted the use of yellow phosphorus. The authors have found this apparatus inconvenient for the preparation of large quantities for which it was not designed, Walker himself advising that not more than 100 grms. of iodine should be operated on at one time. The apparatus illustrated is identical in principle with Walker's, since it depends on solution of iodine by the alcohol, and bringing this solution and not solid iodine into contact with yellow phosphorus. The apparatus figured is about 70 cm. high. The upper end is 2·5 cm. in diameter, and is connected to a 180 cm. condenser of equal diameter. The bottom end is also 2·5 cm. in diameter, and passes through a cork into the 5-litre reaction flask. Bulb *C* is of about 75 c.c. capacity, narrowed at the bottom to a 6 mm. tube, in which is sealed a glass stopcock, *D*, of 2 mm. bore. Bulb *E*, for the reception of the iodine, is of about 1,200 c.c. capacity, and is drawn down at the lower end to a 1 cm. tube holding stopcock *F* of 5 mm. bore. Into the side of bulb *E* is sealed tube *G*, which should be about 2·5 cm. in diameter, 5 to 8 cm. long, and inclined at an angle of 60°. Through the tube *G* is inserted a platinum foil, *H*, perforated with 2 mm. holes, which foil serves to prevent cock *F* being clogged by iodine. Tube *G* is closed by a rubber stopper, pierced by a 6 mm. tube, *J*, drawn to a capillary at its inner end. Among other purposes, this tube serves to equalise the pressure in the apparatus should it be suddenly cooled by draughts, and prevents irregularity in the flow of liquid from *E* to the reaction flask. *K* is a 12 mm. tube for the ascending alcohol vapours, and its upper end must be above the upper end of *L*, a 6 mm. tube, which serves for the return of condensed alcohol in excess of that which it is desired to let flow over the iodine. Stopcock *D* regulates the flow of condensed liquid over the iodine in bulb *E*. Stopcock *F* is generally wide open, except when adding more iodine to *E*. By suitable manipulation of stopcock *F* and the capillary *J*, certain difficulties, due to the fact that the higher alcohols when hot dissolve large quantities of iodine which crystallise out on cooling, and tend to clog the cock *D*, may readily be overcome. The apparatus may be purchased from Paul Anders, Chemistry Building, University of Illinois, Urbana, Ill. G. C. J.



Studies on the American Official Method for Pyridine in Ammonium Nitrate. R. M. Ladd. (*J. Ind. and Eng. Chem.*, 1919, **11**, 552-555.)—The method prescribed by the Acting Chief of Ordnance, War Department, Washington, is reprinted, and experiments are described which show that the results it yields bear no relation whatever to the amount of pyridine present, but measure instead the ammonia which escapes decomposition by the hypobromite.

The following method is shown to be accurate: The sample (250 grms.) is dissolved in 300 c.c. of water in a 1,000 c.c. round-bottomed flask. Methyl orange is added, the solution neutralised with 10 per cent. sodium hydroxide solution, of which an excess of 15 c.c. is then added. The flask, fitted with a spray trap, is connected to a "wash-bottle" containing 300 c.c. of sodium hypobromite solution, made by adding 25 c.c. of bromine to 1,000 c.c. of 10 per cent. sodium hydroxide solution. The "wash-bottle" is made in the form of a test-tube, and is constructed of thin glass, as it has to be heated. It is connected by a spray trap to a condenser. The distillate is collected in 25 c.c. $\frac{N}{10}$ sulphuric acid. The temperature of the hypobromite solution should not exceed 75° C. until nearly all the ammonia driven off has been destroyed. This point is indicated by an acid reaction of the methyl orange in the first flask and by the reduction of the amount of nitrogen escaping from the hypobromite solution. The temperature of the hypobromite solution is now raised to boiling, and 100 c.c. of distillate collected in twenty to twenty-five minutes. The liquid in the receiver is titrated with $\frac{N}{10}$ sodium hydroxide, using first methyl orange and then phenolphthaleïn as indicator. The difference between the two end-points is the measure of the pyridine present, each cubic centimetre corresponding to 0·0079 grm. Test numbers show that the method will estimate percentages of pyridine of the order of 0·1, with an error never exceeding 0·004 per cent. on the sample, or 4 per cent. on the pyridine present. G. C. J.

Proximate Analysis of Wood. W. H. Dore. (*J. Ind. and Eng. Chem.*, 1919, **11**, 556-563.)—Methods for the proximate analysis of woods are described. The author, differing from Cross and Bevan and others, finds sawdust the most satisfactory mechanical condition of wood for purposes of analysis. The objections raised to the use of sawdust have been that it resists penetration by reagents, particularly chlorine gas, and the author overcomes this difficulty by first opening up the pores of the fibre and the space between the fibres by evacuating the container, then allowing the chlorine to be drawn into the vacuum. As the substitution in the fibre progresses more gas is drawn in until the desired reaction is complete, when the flow almost stops. This affords a trustworthy indication of the completeness of the reaction between lignin and chlorine, and makes it easier to arrest the process before secondary reactions, involving the oxidation of cellulose, set in. Since identical results are obtained at room temperature and at 0° C., the author no longer resorts to the artificial cooling which is necessary in the Cross and Bevan process as commonly practised ("Cellulose," 2nd ed., 96).

Using König's method (*Chem. Zeit.*, 1912, **36**, 1101) for lignin, Cross and Bevan's method, modified as above, for cellulose, and usual methods for water, benzene extract, alcohol extract, water extract and hemicellulose (matter soluble in 1 per cent.

sodium hydroxide), the author's figures for Californian coniferous woods total about 97 per cent. Of the Californian hard woods, only 90 per cent. or less is accounted for, and this, the author says, is at least partly due to the nature of the lignin, which is not accurately estimated by König's method. G. C. J.

INORGANIC ANALYSIS.

Analysis of Antimony Salts. (*Revue des Prod. Chem.*, 1919, **22**, 199; *through Chem. News*, 1919, **118**, 275.)—The oldest methods of determining the amount of free sulphur in antimony pentasulphide depended upon the extraction of it by carbon disulphide, using a Soxhlet's apparatus, and it has recently been found that the pentasulphide is practically unattacked in the cold, and even on warming only about 0·4 per cent. is reduced. Benzene or acetone can be used as solvent, but if benzene is used the pentasulphide must previously be thoroughly dried. Acetone is not to be recommended, for it dissolves a small quantity of the sulphide in addition to the free sulphur. Another method of determining the impurities depends upon the fact that antimony pentasulphide is completely soluble in warm ammonia, and the other substances present can be filtered off and determined in the usual way. To estimate the total sulphur the sulphide can be dissolved in a solution of pure potash and then subjected to the action of chlorine, when all the sulphur is transformed into sulphuric acid and the antimony into antimonic acid. Fuming nitric acid can also be used to convert the sulphide into sulphate, which can be estimated as barium sulphate in the usual way, and hydrogen peroxide acts similarly. If the sulphide is dissolved in pure sodium sulphide the percentage of antimony present can be determined by electrolysis, platinum electrodes being employed; but this process cannot be recommended, for the values obtained are always too high. By treating a solution of the sulphide with soda and hydrogen peroxide and adding alcohol, a precipitate of sodium antimonate is obtained after thirty-six hours' standing. From the weight of this precipitate the amount of antimony present can be deduced. In an alternative process the antimony is determined as tetroxide, Sb_2O_4. A given weight of the sulphide is heated over a water-bath with hydrochloric and nitric acids. The solution is evaporated to dryness, taken up with hydrochloric acid, diluted, and filtered. The precipitate consists of silica and calcium sulphate. The antimony is contained in the filtrate, which is decomposed by HCl and oxidised to give Sb_2O_4. H. F. E. H.

Analysis of Fluorspar and of Basic Slags containing Fluorine. G. R. Doyle. (*Chem. News*, 1919, **118**, 304.)—Into a porcelain, silica, or platinum dish is weighed 0·5 grm. of the finely-powdered sample, a little water added to make a paste, followed by 25 c.c. of glacial acetic acid, the mixture being then evaporated nearly to dryness on the water-bath. A further 25 c.c. of acetic acid is added, and the whole is then completely freed from the acid by evaporation to dryness on the water-bath, followed by the steam oven. The residue is taken up in a little hot water, and boiled with about 10 c.c. of water in a beaker for ten minutes, or until the supernatant liquid is clear. If much iron is present, or the sample is dark in colour, the residue left on filtration must be washed back into the dish again, and the acetic acid boiling repeated, the filtrates being then bulked together. The residue (insoluble matter on filtration) contains (*a*) all lime existing as CaF_2, (*b*) most of the silica, (*c*) all iron and alumina; while the filtrate includes (*a*) soluble lime (CaO and $CaCO_3$), (*b*) soluble silica, (*c*) manganese, (*d*) magnesia, (*e*) lead.

This residue is ignited in a platinum dish (but not so strongly as to decompose CaF_2), cooled, and weighed; then treated with hydrofluoric acid and evaporated to dryness, ignited, and weighed again. The loss is SiO_2. To the remaining residue is added 5 c.c. sulphuric acid, the whole being then evaporated to dryness and ignited. The gain in weight is the increase of $CaSO_4$ over CaF_2. The residue is next boiled for twenty minutes with hydrochloric acid, ammonia and ammonium chloride added, again boiled and filtered. In the presence of much iron and alumina, precipitation is carried out again. The residue of iron and alumina is ignited and weighed and deducted from the combined weight of Fe, Al, and CaF_2. The difference is CaF_2. If lead be present, it must be removed by sulphuretted hydrogen before the precipitation of iron and aluminium. After Fe and Al have been weighed, the assay is dissolved, reduced, and titrated, the alumina being thence determined by difference.

The filtrate is evaporated to dryness with 5 c.c. of hydrochloric acid and 3 drops of nitric acid, the silica finally obtained being added to that found in the residue. If lead is found in the filtrate from the SiO_2 it is removed with sulphuretted hydrogen, the manganese being then weighed as Mn_3O_4 after treating the filtrate with ammonium chloride, bromine to saturation, and ammonia. The filtrate is then boiled with ammonium oxalate to separate lime, magnesia being finally precipitated with ammonium phosphate. H. F. E. H.

New Microchemical Reaction for Gold, Silver, and Rubidium. F. Emich. (*Chem. Zeit.*, 1919, **43**, 203.)—When a solution of gold chloride is mixed with silver chloride and rubidium chloride, blood-red crystals of probably a triple chloride are produced. The reaction may be used for the microchemical detection of gold and silver, and conversely of rubidium, cæsium, or potassium, the two last being capable of replacing rubidium in the test. The compounds, which appear to be analogous with triple nitrites of the type of copper-lead-potassium nitrite, are only sparingly soluble, and are not decomposed by acetic acid. C. A. M.

Estimation of Iodide in Mineral Waters and Brines. W. F. Baughman and W. W. Skinner. (*J. Ind. and Eng. Chem.*, 1919, **11**, 563-568.)—Of the sample so much is taken as will contain not more than 0·1 grm. iodine nor more than 10 grms. total salts. The solution is concentrated or diluted to 100 c.c. and boiled with sufficient sodium hydroxide and carbonate to precipitate calcium and magnesium. The filtrate and washings are concentrated to 100 c.c., neutralised with sulphuric acid, and 1 c.c. of 4 per cent. sodium hydroxide solution is added. The solution is heated to boiling, excess of permanganate added to convert iodide to iodate, and heating continued until the precipitate flocculates. When cool, the excess of permanganate is destroyed by addition of alcohol. The solution is then filtered and 1 grm. or more potassium iodide is added to the filtrate, which is acidified with hydrochloric acid and titrated with $\frac{N}{10}$ thiosulphate, of which 1 c.c. corresponds to only 0·002115 grm. iodine in the sample, since for every molecule of iodide in the sample there are six atoms of iodine in the mixture finally titrated. G. C. J.

Estimation of Iodides. P. Godfrin. (*J. Pharm. Chim.*, 1919, [vii.] **19**, 445-450.)—The method described is based on the reaction between iodides and potassium dichromate in the presence of hydrochloric acid. Ten c.c. of an approximately 1 per cent. solution of the iodide are treated with 1 c.c. of 10 per cent. potassium dichromate solution and 15 drops of hydrochloric acid; after thirty seconds, 20 c.c. of 10 per cent. sodium acetate solution, 2 c.c. of starch solution, and 50 c.c. of water are added, and the iodine is titrated with thiosulphate solution. The method may be applied to the estimation of iodide in urine. To destroy substances which absorb iodine, the sample is first titrated with dilute iodine solution, using starch as indicator, and the process is then carried out as described; but three minutes must elapse after the dichromate has been added and before the addition of the sodium acetate. W. P. S.

Sensitive Reaction of Manganese Salts. H. Caron and D. Raquet. (*Ann. Chim. Anal. appl.*, 1919, **1**, 174.)—On treating an acidified solution of manganese salts with an excess of an alkali oxalate, preferably potassium oxalate, and an oxidising agent, such as a dichromate, hypochlorite, or peroxide, an intense gooseberry-red coloration is produced, owing to the formation of a double oxalate of manganese and alkali. Ten c.c. of the solution are treated with 2 c.c. of a cold saturated solution of potassium oxalate, 1 c.c. of acetic acid, and 1 drop of a solution of potassium dichromate or of hydrogen peroxide, and the coloration is obtained in the presence of 0·1 to 0·5 mgrm. of manganese. By using an alkali hypochlorite as the oxidising agent the reaction is rendered more sensitive, and is capable of detecting 0·05 mgrm. in 10 c.c. The coloration is also better suited for colorimetric estimation. Iron, if present to any notable extent, interferes with the test, but zinc does not affect the result provided that sufficient acetic acid is added to dissolve the precipitate of zinc oxalate. C. A. M.

Use of Colloidal Silicic Acid in Titration of Iron by Means of Permanganate. E. Dittler. (*Chem. Zeit.*, 1919, **43**, 262.)—The author confirms the conclusions of Schwarz and Rolfes (ANALYST, 1919, 181) that the presence of a sufficient quantity of colloidal silicic acid wholly inhibits the oxidation of hydrochloric acid when iron is titrated with permanganate in presence of Reinhardt's manganese mixture. He recommends a proprietary preparation of silicic acid ("Osmosil," manufactured by the Electro-Osmose A.-G., Vienna) as superior to the ordinary water-glass of commerce because, he says, the latter readily flocculates and becomes useless for this purpose. G. C. J.

APPARATUS, ETC.

Apparatus for the Rapid Analysis of Air in Rooms, etc. E. Kohn-Abrest. (*Comptes rend.*, 1919, **168**, 1019-1022.)—The apparatus consists of a 5-litre aspirator, the upper part of which is connected separately with a number of absorption flasks containing suitable reagent solutions. Carbon dioxide is estimated by aspirating a given volume of air, at the rate of 120 bubbles per minute, through the flask containing barium hydroxide solution; the quantity of carbon dioxide can be ascertained approximately by noting the time required to produce a distinct turbidity or precipitate in the solution. For instance, twenty minutes is required in the case of air containing 5 parts of carbon dioxide per 10,000, or ten minutes with air containing 1 part per 1,000. An iodine pentoxide tube, heated electrically, is provided for the estimation of carbon monoxide; the air is passed previously through barium hydroxide solution, and any carbon dioxide formed from the carbon moxoxide is collected in barium hydroxide solution contained in a flask placed between the tube and the aspirator. W. P. S.

Apparatus for Accurate Calibration of Burette Tubes. S. English. (*J. Soc. Glass Technol.*, 1919, **3**, 34-37; through *J. Soc. Chem. Ind.*, 1919, **38**, 481 A.). —The burette tube is connected through a tap-tube to an elevated mercury reservoir and to an accurately calibrated 10 c.c. pipette fitted with a three-way tap. The burette tube is nearly filled with mercury and about 1 c.c. of water is then poured in so as to wet the sides as the mercury is withdrawn into the pipette. The position of the water-meniscus in the burette after each successive 10 c.c. has been withdrawn is made to coincide with the cross wire in a short-focus telescope mounted on a vertical support which is exactly parallel to the burette. A mark is then made on the tube with a fine needle pivoted near the front of the telescope in such a manner that this mark exactly coincides with the level of the cross wire in the telescope. By this means it is impossible to make a mark in a wrong position or with an error due to parallax. It is essential to use the same background in each case and to fix it at the same distance from the burette. If the apparatus faces a window or light a screen of ground glass is recommended, but if the apparatus faces away from the light a white tile is preferable. The mean difference per 10 c.c. in calibrating a 50 c.c. burette as described and by weighing successive lots of 10 c.c. of water is 0·0004 grm. The calibration of five sections of 10 c.c. each may be completed in less than five minutes.

Comparative Tests of "Palan" and "Rhotanium" Ware as Substitutes for Platinum Laboratory Utensils. L. J. Gurevich and E. Wichers. (*J. Ind. and Eng. Chem.*, 1919, **11**, 570-573.)—Palan and rhotanium are alloys of gold and palladium, the former containing 20 per cent. of palladium, whilst rhotanium is made with varying proportions of palladium, the crucibles submitted to the United States Bureau of Standards, whence this communication comes, being made of rhotanium A (10 per cent. Pd) and rhotanium C (30 per cent. Pd).

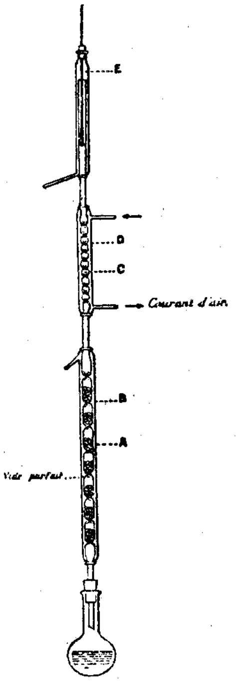
Rhotanium A is superior to platinum in respect to its resistance to loss on heating, compares favourably with platinum in resistance to boiling hydrochloric and hydrofluoric acids, to boiling 20 per cent. sodium hydroxide, to fusion with sodium carbonate and with potassium pyrosulphate. It is superior to platinum in resistance to boiling sulphuric acid, but inferior in its resistance to nitric acid, boiling ferric chloride solution and for fusions with sodium hydroxide. The low m.p. of the alloy is a disadvantage.

As far as resistance to loss of weight on heating is concerned, rhotanium C and palan are at least equal to platinum. Towards reagents they behave similarly to rhotanium A, except that they are not suitable for pyrosulphate fusions and are inferior to grade A for hydroxide fusions.

All these alloys can be employed as cathodes in the electrolysis of solutions. As anodes they are worthless.

The authors have not had these utensils in use long enough to state from personal knowledge how they behave in actual service. They are anxious to obtain reports from chemists who have used utensils made from these alloys. Already they have heard of crucibles cracking after a few months' service. G. C. J.

Rapid Filter for Use in the Estimation of Crude Fibre, etc. F. Mach and P. Lederle. (*Chem. Zeit.*, 1919, **43**, 251.)—The filter consists of a perforated porcelain plate on which rests a disc of platinum gauze; the latter has meshes about 0·5 mm. in diameter and has 16 to 17 meshes per cm. A layer of washed asbestos fibre is placed on the gauze. W. P. S.



New Fractionating Column. H. Robert. (*Comptes rend.*, 1919, **168**, 998-1001.)—The bulb tube constituting the lower part of the column (see figure) is provided with a jacket from which the air is exhausted as completely as possible; the bulbs themselves are formed by making a number of constrictions on the tube and each bulb contains a number of small glass cylinders about 8 mm. in diameter and of the same height. The middle portion of the column consists of a bulb tube also provided with a jacket through which a current of air is drawn, whilst the upper part of the column consists of a double tube, the vapours passing up the central tube and then downwards to the side tube leading to the condenser. It is claimed that, by the use of this column, a single distillation of 50 per cent. alcohol will yield a distillate containing 93 per cent. of the alcohol in the form of 96 per cent. alcohol. Further, pentane, hexane, and heptane may be fractionated from petrol, 80 per cent. of pure anhydride may be obtained from a mixture of acetic anhydride and acetic acid, etc. W. P. S.

Precision Pressure Gauge. E. J. Brady. (*Chem. News*, 1919, **118**, 267.) In principle the apparatus is a U-tube (6 c.c. diameter) filled with some transparent non-volatile non-oxidising liquid such as kerosene. In each limb is placed a hollow brass float, these being connected by means of a fine silk thread which passes downwards around a light graduated wheel with jewelled bearings immersed in oil at the bottom. The position of this wheel, which is provided with a vernier, is read through a glass window in one end of the box that forms the bottom of the gauge. Owing to its sensitiveness to very small pressures, the gauge should increase the usefulness of both the Venturi meter and the Pitot tube. Any pressure P on the liquid in one of the tubes produces a linear motion $\frac{P}{2}$ at the circumference of the wheel around which passes the silk thread. The diameter of this wheel is so chosen that a pressure of 1 inch of distilled water on kerosene produces a motion of the periphery of the wheel of ten divisions. By suitable minor adjustments described in detail pressure differences of less than 10^{-3} inches of water can be recorded. The friction of the wheel may be made as near zero as possible by making it of aluminium, and so proportioning it that its weight *in the oil used* is just equal to the buoyancy of the two floats. H. F. E. H.

Use of the Refractometer in the Examination of Ethylene Chlorhydrin. A. E. Berry. (*J. Soc. Chem. Ind.*, 1919, **38**, 145-146T.)—In the distillation of aqueous ethylene chlorhydrin solutions the refractive index of the distillate gives a reliable indication of the amount of the chlorhydrin in the distilled mixture. The refractive index of a 20 per cent. chlorhydrin solution (in water) is 1·3554; that of a 10 per cent. solution 1·3444; whilst that of water is 1·3334. There is thus a linear relationship between the chlorhydrin content and the refractive index.

W. P. S.

Use of the Refractometer in the Estimation of the Protein Content of Sera. A. Homer. (*J. Soc. Chem. Ind.*, 1919, **38**, 145T.)—The refractive index of the solution is determined at 17·5° C. by means of the immersion refractometer; the solution is then heated in a closed tube at 100° C. for five minutes to coagulate the protein, cooled, filtered, and the refractive index of the filtrate determined. The difference between the two readings gives the scale index reading for the protein constituent. Better separation of the coagulated protein is obtained if the serum, before heating, is mixed with its own volume of 2 per cent. sodium chloride solution; allowance for the refractive index of the salt thus introduced and the dilution must be made. W. P. S.

Refractometer in the Sugar Industry. H. Main. (*J. Soc. Chem. Ind.*, 1919, **38**, 143-145T.)—Attention is drawn to the use of the refractometer in estimating the strength of sugar solutions; the author refers to work published by Herzfeld, Geerligs, Lange, Tolman, and Smith, Stanek, Wagner, and himself. Most of the tables showing refractive indices of sugar solutions, etc., have been brought together and published in Circular No. 4, Bureau of Standards, Washington, U.S.A. (See also Miller and Worley, ANALYST, 1918, **43**, 221). W. P. S.

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REVIEWS.

MODERN CHEMISTRY AND CHEMICAL INDUSTRY OF STARCH AND CELLULOSE (WITH REFERENCE TO INDIA). By TARINI CHARAN CHAUDHURI, M.A. 1918. London. Butterworth and Co. Rs. 3.12. Pp. 150.

It is to be feared that this little book is not one that can be recommended to the favourable notice of the industrial chemist, or even to the layman connected with this branch of industry; for not only is it devoid of all precise information on the analytical and manufacturing side of the subjects dealt with, but it is inadequate and superficial in its general treatment of the enormous field to be surveyed. The quaint exotic "English" of the author is frequently employed in a manner more suitable to some volume in a "Peeps at Nature's Marvels" series than to a serious contribution to chemical literature, while misprints and errors of varying kinds are abundant. Of cellulose we read: "Its application may range from the manufacture of cellulose-coffins to cellulose-whiskey—[Cause and effect would suggest an inversion of this order. *Reviewer*]—from steamer stewards bad weather-basins [*sic*] to fine cellulose-suits, which are more strong and durable than ordinary cellulosic stuffs. A London firm has already launched upon making textiles of various description from pure cellulose with nice shades of colour."

The manufacture of nitro-explosives, collodion, celluloid, artificial rubber and silk, acetone, gas mantles, sugar and starch products, are all described or touched upon, though it may be doubted whether starch finds the "extensive use in condensed milk manufacture" which the author claims for it. Confirmation is surely lacking, too, for the statement on p. 15 that Aubert's and Giraud's claim to have made cane-sugar by passing an electric current at 100° C. through acidified starch-paste "has been certified by subsequent investigators, and may be received without any qualification."

The index is a complete one, while numerous footnotes refer the reader to a curious medley of original articles, books, patents, and journals in all languages.

HENRY F. EVERARD HULTON.

TABLES OF REFRACTIVE INDICES. Vol. I.: Essential Oils. Compiled by R. Kanthack. Edited by J. N. Goldsmith, Ph.D., M.Sc., F.I.C. Adam Hilger, Ltd. London, 1918. Pp. 148. Price 15s. 4d., post free.

These tables deal with over 500 distinct oils, and record some 1,500 measurements, which have been abstracted from many sources. References are given not only to the original papers, but also to the abstracts in other journals. It is not the fault of the Editor or the Compiler that the readings have been taken at a great variety of temperatures; they must rather be complimented upon the care with which they have arranged the available data.

The work presents the reader with valuable data from the past, and it is to be hoped that by so doing it will form a nucleus for the expansion of much-needed records.

E. RICHARDS BOLTON.