

# THE ANALYST

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

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An Ordinary meeting of the Society was held on Wednesday, March 4th, at the Chemical Society's Rooms, Burlington House. The President, Mr. G. Rudd Thompson, F.I.C., was in the chair.

Certificates were read for the first time in favour of:—Messrs. George William Fraser Holroyd, M.A. (Oxon), F.I.C., Cecil Eric Keeley, Andrew Francis Macculloch, M.A., B.Sc. (Edin.), A.I.C., Frank Vegetus North Mitchell, Charles Henry Thomson, and Walter Peter Whitley, B.A. (Oxon.).

Certificates were read for the second time in favour of:—Messrs. Douglas James Talbot Bagnall, A.C.G.F.C., A.I.C., Reginald Henry Coysh, M.Sc., A.I.C., George Van Barneveld Gilmour, B.Sc., A.R.C.Sc.I., A.I.C., Percy May, D.Sc., F.I.C., John Parry, Wilfrid Smith, B.Sc., A.I.C., and Miss Winifred Wright, B.Sc., A.I.C.

Mr. Thomas Mann was elected a Member of the Society.

The following papers were read:—"A New Method for the Determination of Butter Fat," by G. Van B. Gilmour, B.Sc., A.R.C.Sc.I., A.I.C.; "The Investigation of Ventilation Conditions," by R. C. Frederick; "A Simple and Self-Contained Spectroscope Lighting Unit," by R. C. Frederick and E. R. Webster (with demonstration of apparatus); and "The Carbon Error in the Quantitative Deposition of Nickel and Iron from Complex Oxalate Electrolytes," by P. K. Fröhlich.

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### Deaths.

With deep regret we record the death of two of our Members—Sir Edward Thorpe, F.R.S., on February 23rd, and R. Atkinson Oddy, on March 12th.

## Cinchonine as a Tannin Precipitant with Special Reference to the Analysis of Cutch and Gambier.

By DAVID HOOPER, LL.D., F.I.C.

[*Investigation carried out under the Society's Analytical Investigation Scheme.*]

(*Read at the Meeting, February 4, 1925.*)

PRECIPITATION OF TANNINS WITH ALKALOIDS.—The formation of a precipitate when alkaloidal salts are added to a solution of tannin is a well known qualitative reaction, and quinine, quinidine, cinchonine and strychnine have, at various times, been recommended as reagents. Wagner (*Zeitsch. anal. Chem.*, 1867, **5**, 1), for instance, employed cinchonine in determining tannin quantitatively, but the results of his experiments were considered too low and unreliable. Trotman and Hackford (*J. Soc. Chem. Ind.*, 1905, **24**, 1098) carried out an interesting investigation, in which the alkaloid strychnine was used as a tannin precipitant, and from the weight of the precipitate the amount of tannin was estimated in sumach and other materials. On the whole, the results were lower than those obtained by the hide powder method.

More recently, A. Chaston Chapman (*J. Inst. Brewing*, 1907, **13**, 646-657; 1909, **15**, 360-374) devised a method to determine the amount of tannin in hops by means of cinchonine. Concordant duplicate analyses of various descriptions of Continental and English hops yielded from 1.83 to 3.68 per cent. of tannin, calculated from the weight of dried cinchonine tannate. Following on these results, Henry L. Smith, under the Investigation Scheme of the Society of Public Analysts, published a paper on "The Determination of Tannin in Tea" (*ANALYST*, 1913, **39**, 312-316), giving the details of an investigation in which cinchonine sulphate was used as the precipitating agent. The percentage of tannin in a few commercial samples of tea ranged from 12 in one from China to 16.9 in an Indian grade. Procter's modification of Löwenthal's permanganate method gave lower results in each case.

Since writing his paper, Chapman has used the cinchonine method with very useful results in the examination of materials other than hops. He has also suggested that a systematic enquiry should be made with the object of ascertaining to what extent the cinchonine method is applicable to miscellaneous tanning materials in general. It was also considered desirable to compare the results with those obtained by a standard method of tannin analysis. The work embodied in the present paper gives the results of this enquiry.

**THE CINCHONINE METHOD.**—The cinchonine sulphate employed in the experiments had a composition corresponding with the formula  $2(C_{19}H_{22}ON_2) \cdot H_2SO_4$ , and was used in the form of a saturated aqueous solution, one hundred parts of which yielded on evaporation 1.3 parts of anhydrous salt.

In applying this test, solutions were made of tannins and tanning materials available in the laboratory. The hide powder method was applied to the examination of each sample, and this was carried out according to the instructions in Procter's *Leather Industries Laboratory Book*. The extracts were made so as to contain about 4 grms. of soluble tanning matter per litre, which strength was regarded as the optimum for the cinchonine method. After measuring off what was required for total solids and hide powder, portions of 50 c.c. were measured off in triplicate and treated with 50 c.c. of cinchonine sulphate solution. The precipitates were allowed to stand and aggregate for at least an hour. For the purpose of filtration a series of alundum crucibles was used, each of which was ignited before use, moistened with a solution of cinchonine sulphate (the saturated solution mixed with an equal volume of distilled water), and dried to constant weight. The precipitate was then poured into the crucible and allowed to filter, at first without suction, then with the aid of a pump. When all the liquid was filtered through, the precipitate was washed with some of the half-saturated solution, and suction continued until no more liquid was removed. The crucibles with precipitates were placed on a porous plate till next day, when they were thoroughly dried in a water-oven and weighed. It must be emphasised that, if the damp precipitate is dried in the oven, it fuses to a brown or black mass giving inconstant results, but when dried, first in the air then in an oven, very concordant results are obtained.

**COMPOSITION OF CINCHONINE TANNATES.**—The composition of the cinchonine tannates is of importance in this method of analysis, since this gives the requisite factor for calculating the amount of tannin. Chapman found that cinchonine gallotannate yielded, according to Dumas' method, 3.45 per cent. of nitrogen, corresponding to 36.2 per cent. of alkaloid and 63.8 per cent. of tannin. He also found that lupulotannate contained 4.3 per cent. of nitrogen, corresponding to 45.1 per cent. of cinchonine and 54.9 (practically 55) per cent. of tannin. H. L. Smith, by combustion of the precipitated cinchonine tannate from tea, obtained 4.3 per cent. of nitrogen and used the same factor, namely 55.

To test these figures further a sample of gallotannin specially purified by Nierenstein's method (*Annalen*, 1912, 388, 223) was taken for experiment. It was composed of water, 11.1; gallic acid, 1.9; determined by Mitchell's colorimetric method modified by Nicholson and Rhind (*ANALYST*, 1924, 49, 505); tannin (by difference) 87 per cent. Washed hide powder absorbed as much as 84 to 85 per cent. of this material. Quantities of 0.1 grm. in solution precipitated with cinchonine sulphate yielded, on an average, 0.140 grm. of dried cinchonine tannate. The amount of nitrogen obtained by Dumas' method was 3.9 per cent., showing 40 per cent. of alkaloid; the corresponding factor 0.6 represents 84 per cent. of tannin in the sample. There seems to be a satisfactory agreement between the

two methods, although neither of them fully accounts for the 87 per cent. of tannin, or whatever that body represents, in the purified gallotannin.

Another experiment was made on a sample of commercially pure gallotannin which showed, on analysis by Mitchell's colorimetric method, the following composition:—Water, 11.5; gallic acid, 10.7; tannin by difference, 77.8.

The hide powder method indicated as much as 76.8 parts of tannin. A large number of weighings of the precipitate obtained by adding an excess of cinchonine sulphate to 0.1 grm. of the substance, averaged 0.128 grm. The nitrogen content was 3.87, giving a factor of 0.6, corresponding to 76.8 per cent. of tannin. Again, there is a close agreement between the two methods of analysis when operating on a fairly pure astringent principle.

**TANNIN IN CRUDE TANNING MATERIALS.**—Attention was next directed to the determination of tannin in various crude tanning materials well known in the market. The hide powder method, with due precautions, and the cinchonine method, as detailed above, were applied to each. Each figure in the first two columns in the following table is the result of several determinations.

Name.	Tannin by Hide Powder.	Tannin by Cinchonine Sulphate.	No. of determinations by Cinchonine.	*N in Cinchonine Tannate.	Factor.†
Quebracho extract	70.4	67.2	6	3.8	0.60
China galls	61.2	60.5	6	3.5	0.63
Bagdad galls	59.6	58.6	6	—	0.63
Mangrove bark	28.5	20.2	6	2.4	0.75
Sumach	24.0	23.0	9	3.9	0.59
Mimosa bark	24.0	14.3	6	3.5	0.63
Myrobalans	22.8	20.9	9	3.4	0.64
Kino, Indian	28.8	24.9	9	3.2	0.66
Kino, Eucalyptus	20.4	16.3	9	3.5	0.63
Cube gambier	40.4	10.0	15	3.8	0.60
Acacia cat. wood	6.7	3.7	15	3.5	0.63
Tea	13.0	12.6	6	4.3‡	0.55
Oak bark	7.1	5.3	9	3.5	0.63

In the above table it will be noticed that with the richer tanning materials, such as galls, quebracho extract, myrobalans and sumach, there is a fairly close correspondence between the two methods of analysis employed. With the less astringent matters, such as the barks of mangrove, mimosa and oak, there is a greater divergence, and the purchaser of tan barks would prefer to buy his material on the results obtained by the cinchonine method rather than on those obtained by the hide powder method. It is possible that the lower results of the cinchonine

\* I am indebted to Mr. C. J. Cordy, B.Sc., of this University, for determining, by the Dumas method, the percentage of nitrogen in each tannate.

† The factor is obtained by dividing the percentage of N by 9.52, and the cinchonine so found is subtracted from the tannate to give the proportion of tannin.

‡ The figure for N found by H. L. Smith (*loc. cit.*).



The catechin was separated and determined by crystallisation from an aqueous solution of the alcoholic extract, the mother liquors being evaporated, and the catechin separated as long as any crystals formed. This method was used by the author in finding the percentage of catechin in a large number of samples of cutch examined in India (*Agricultural Ledger*, No. 3, 1906). The figures in the present instance were confirmed by evaporating and separating the crystals from the aqueous solution of the ethyl acetate extracts.

There appears to be no definite ratio between catechin and tannin in these commercial samples of cutch. In 1 and 2 the catechin is more than double the amount of tannin, and the proportion is reversed in 4 and 7; in No. 5 the catechin and tannin are nearly equally balanced. The results of the hide powder method are not given in the above table since they include catechin. It must be conceded that the analysis showing the catechin separated in a crystalline condition, and the tannin determined by cinchonine, shows the composition of cutch in a better way than the usual method of analysis.

These experiments indicate that although cinchonine sulphate is only a fairly good quantitative precipitant of tannin in certain tanning materials, it may have special value in determining tannin in the presence of catechin.

The author's thanks are due to Dr. Nierenstein for the interest he has shown in the work and the advice he has given.

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#### DISCUSSION.

Mr. CHASTON CHAPMAN writes: "It is, of course, very gratifying to me to find that my cinchonine method has given such good results in Dr. Hooper's hands. That it is specially useful in the analysis of certain natural products and commercial extracts containing both tannin and catechin I have known for a considerable time, and I have, on several occasions, employed it in the examination of catechu and similar materials. In such products the results for tannin are, of course, much lower than by the hide powder process, since the cinchonine method gives the true tannin, whereas the hide powder gives the combined percentage of all materials removable by that reagent.

It is interesting to observe that the nitrogen percentage which I found in the cinchonine lupulo-tannate is very nearly that found by Dr. Hooper in the corresponding compound with gallotannic acid, namely, 4.3 per cent. It seems that a study of the cinchonine compounds of the various so-called tannic acids might help materially to an understanding of the true nature of those substances."

# On the Absorption of Carbon Monoxide.

## PART I.

### A Critical Comparison of some Methods Employed in Gas Analysis.

By H. R. AMBLER, B.Sc., A.I.C.

(Read at the Meeting, February 4, 1925.)

THE absorption of carbon monoxide by cuprous chloride is frequently found to be not strictly quantitative. In this paper are investigated:

- (A) The conditions governing the absorption of carbon monoxide by cuprous chloride. (a) Dissolved in hydrochloric acid; (b) Dissolved in ammonia.
- (B) The use of a suspension of cuprous oxide in sulphuric acid containing  $\beta$ -naphthol, as an alternative and an improvement.

Attention has been directed particularly to:—(1) Completeness of absorption; (2) rate of absorption; (3) the effect, on the absorptive power, of carbon monoxide previously absorbed.

The apparatus used was of the Sodeau (constant pressure) type. The experiments were all conducted at atmospheric temperature.

ACID SOLUTION OF CUPROUS CHLORIDE.—This solution is prepared by dissolving 30 grms. of cuprous chloride in a mixture of 50 c.c. of water and 150 c.c. of concentrated hydrochloric acid. The solution is then kept in an air-tight bottle with a spiral of copper wire until the brown colour, due to cupric chloride, has disappeared.\*

It was found that this solution did not absorb carbon monoxide completely. For instance, gas samples known to contain between 0.5 and 0.8 per cent. of methane† gave apparent percentages as high as 1.3, even when the gas had been shaken successively in three absorption pipettes, each containing fresh solution.

An artificial mixture of nitrogen, carbon monoxide and hydrogen (containing no methane) was analysed, with the following results:

	c.c.	c.c.
Volume of original gas (c.c.)	42.2	44.85
Volume after shaking with (old) solution No. 1	22.5	24.7
Volume after shaking, solution No. 2 (had previously absorbed about 4 c.c.)	21.9	23.5
Volume after shaking, solution No. 3 (fresh)	21.8	23.35
Volume after addition of oxygen	30.6	32.50
Volume after explosion	9.7	10.30
Volume after shaking with potash	9.35	10.00
Volume of carbon monoxide left unabsorbed	0.35	0.30

\* If cupric chloride is present the solution is not markedly less efficient, but cannot be kept in contact with mercury in the absorption pipettes.

† Methane is determined by measuring the carbon dioxide produced by its combustion, which is carried out (together with that of hydrogen) after the removal of carbon monoxide. Any carbon monoxide left unabsorbed will, of course, be determined as methane.

*Rate of absorption and vapour-pressure of acid.*—It is often stated that it is necessary to leave the gas in contact with the solution for as long as 10 minutes. It appears, however, that any carbon monoxide left unabsorbed after one minute's shaking will not be absorbed after any further contact with the same solution.

This is shown in the following analysis:

	c.c.	c.c.
Volume of gas after removal of CO <sub>2</sub> and oxygen .. .. .	28.55	33.70
Volume of gas after shaking $\frac{1}{2}$ minute with cuprous chloride .. .. .	15.60	12.85
Volume after standing 20 minutes with cuprous chloride .. .. .	15.60	—
Volume after standing 30 minutes with cuprous chloride .. .. .	—	12.90

The slight increase in volume in the second case is probably due to increase in the vapour pressure of the hydrochloric acid; the volume reading, however, is not accurate, to much closer than 0.05 c.c.

For practical purposes this vapour pressure is negligible, as, *e.g.* in the following results:

	(1)	(2)	(3)
	c.c.	c.c.	c.c.
Volume after shaking with cuprous chloride .. .. .	19.95	15.55	19.80
Volume after shaking with water .. .. .	19.90	15.50	19.80

It is unnecessary, therefore, to wash the gas with water after acid cuprous chloride, especially as the errors due to incomplete absorption are of a much higher order than this vapour pressure effect.

**AMMONIACAL SOLUTION OF CUPROUS CHLORIDE.**—The solution is prepared by passing ammonia gas through a suspension of 20 grms. of cuprous chloride in 150 c.c. of water, in absence of air. The solution prepared under ordinary conditions, either from stock cuprous chloride or from the fully reduced precipitated compound is of a fairly deep blue colour, becoming lighter as it takes up carbon monoxide, until it becomes almost colourless. This loss of colour is a useful indication that the solution is becoming exhausted, as at about this point it begins to show a loss in efficiency. It is to be noted that if, in the preparation, care is not taken to exclude air, a solution is obtained of the same colour and showing the same colour change with use, but which is much less efficient.

Ammoniacal cuprous chloride, even when considerably oxidised, can be kept in contact with mercury indefinitely. It was found to be a considerable improvement on the acid solution, as is seen in the following results:

	c.c.
Volume of gas after shaking successively with three fresh acid CuCl solutions .. .. .	15.50
Volume after shaking with water .. .. .	15.50
Volume after shaking with ammoniacal cuprous chloride .. .. .	15.10
Volume after shaking with water .. .. .	15.15

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Volume left unabsorbed by acid solution but absorbed by ammoniacal solution .. .. . 0.35



When tested with the methane-free mixture it was found to absorb the carbon monoxide completely:

	c.c.
Original volume .. .. .	41.95
Volume after shaking with ammoniacal solution (1) .. .. .	23.35
Volume after shaking with ammoniacal solution (2) (fresh) .. .. .	23.15
Volume after shaking with water .. .. .	23.05
Volume after addition of oxygen .. .. .	33.8
Volume after explosion .. .. .	14.2
Volume after shaking with potash .. .. .	14.2
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Volume of CO not absorbed .. .. .	Nil

A similar experiment on a different methane-free mixture gave 0.03 c.c., *i.e.* 0.06 per cent. of apparent methane, a figure within the limits of accuracy of reading.

For routine analysis three successive absorbers filled with the above solution are used; if, on shaking, any further contraction occurs in the third, the first is refilled with fresh solution and used as "No. 3," Nos. "2" and "3" becoming "1" and "2" respectively in rotation. This procedure ensures that the solution in the third pipette has not previously absorbed any carbon monoxide—a condition necessary to prevent incomplete absorption later.

*Rate of absorption and vapour pressure of ammonia.*—As in the case of the acid solution, 1 minute is sufficient for the absorption to take place, as is shown below. The effect of keeping the gases in contact with the solution is sometimes an increase of volume due to the vapour pressure of ammonia; this may be considerably greater than that of the hydrochloric acid in the acid solution. For this reason the gas should always be washed, after absorption of carbon monoxide, in a pipette filled with water. The magnitude of this effect varies with the details of preparation of the solution; it may be as small as 0.05 c.c., or as great as 1 c.c. The following results are examples showing the rate of absorption and the magnitude of the vapour pressure effect.

	c.c.	c.c.		
Volume after shaking 15 seconds with solution .. .. .		37.20		
Volume after shaking 1 minute with same solution .. .. .		37.30	{ No further absorption of CO	
Volume after standing 5 minutes with same solution .. .. .	23.00			
Volume after standing ½ hour .. .. .	23.15			
Volume after washing with water .. .. .	23.05	0.1 c.c. of NH <sub>3</sub> No further absorption of CO	36.3	1 c.c. of NH <sub>3</sub>

Volume after removal of CO <sub>2</sub> and oxygen.	c.c. 38.25	
Volume after shaking 30 seconds with CuCl solution (1).	19.95	Volume of CO absorbed in first 30 seconds = 18.45 c.c., <i>i.e.</i> 99 per cent. of the total absorption in 4 minutes by same solution.
Volume after shaking with water.	19.80	0.15 c.c. NH <sub>3</sub> gas evolved by solution.
Volume after shaking 30 seconds with CuCl solution (1).	19.85	Volume of CO absorbed in second 30 secs. = 0.12 c.c. Volume absorbed in 1st minute = 18.57 c.c.
Volume after shaking with water.	19.68	0.17 c.c. NH <sub>3</sub> gas evolved by solution.
Volume after shaking 3 mins. with CuCl solution (1).	19.82	0.03 c.c. removed (a figure within the limits of reading error), <i>i.e.</i> practically all the CO is absorbed in the first minute.
Volume after shaking with water.	19.65	0.17 c.c. NH <sub>3</sub> gas evolved by solution.
Volume after shaking 30 seconds with CuCl solution (2) (fresh).	19.60	A further 0.13 c.c. absorbed by fresh solution in 30 seconds.
Volume after shaking with water.	19.52	0.18 c.c. NH <sub>3</sub> gas evolved by solution.

CUPROUS OXIDE IN SULPHURIC ACID CONTAINING  $\beta$ -NAPHTHOL.—Lebeau and Bedel (*Compt. Rend.*, 1924, 179, 108; *ANALYST*, 1924, 49, 451) recommend a suspension of cuprous oxide in sulphuric acid containing  $\beta$ -naphthol. Although, as the discoverers point out, the reagent can be kept in contact with mercury, a slow reaction appears to take place, with the evolution of gas amounting to about 0.02 c.c. of gas per hour per 100 c.c. of solution. This gas is absorbed by potassium hydroxide and is probably hydrogen sulphide, since the used solution has a faint odour of this gas. This effect can be greatly diminished by not using mercury in the pipette and, instead, protecting the surface of the liquid in the upper part of the pipette with a layer of B.P. paraffin. With absorption pipettes, such as that of Sodeau, in which the absorbent is kept in the pipette, this procedure is to be advised. Even with this precaution, however, the gas should always be shaken subsequently with water or potash.

The results obtained here show that the solution gives quantitative absorption of carbon monoxide within the limits of measuring error. Its efficiency, moreover, (unlike that of cuprous chloride) is not impaired by the previous absorption of considerable quantities of carbon monoxide.

*Rate of absorption.*—The rate of absorption is lower than that of cuprous chloride, and is also largely governed by the amount of shaking.\*

\* That this slowness of absorption and necessity for shaking was not due to the covering of the surface of liquid in the lower part of the pipette with a film of B.P. paraffin, is shown by the fact that similar results were obtained with the use of a pipette (containing mercury) from which B.P. paraffin was excluded.

The properties of this solution as regards the absorption of CO are demonstrated in the following experiments:

Volume of gas after removal of CO <sub>2</sub> and oxygen		c.c.	
		42·89	
Volume after shaking with Cu <sub>2</sub> O suspension which had previously absorbed 50 c.c. of CO	{ 3 mins. " " " " " "	25·36	76 per cent. absorbed.
		20·12	98·5 " "
		20·06	99·2 " "
		20·01	100 " "
		20·01	100 " "
Volume after shaking 5 minutes with fresh suspension.		20·01	No further CO removed.
Volume after shaking with water.		19·82	Gases produced by absorbent removed.
Volume after shaking with fresh ammoniacal cuprous chloride.		20·13	Increase due to V.P. of NH <sub>3</sub> .
Volume after shaking with water.		19·82	0·32 c.c. of NH <sub>3</sub> removed.
<i>i.e.</i> Volume of CO not absorbed by solution which had previously absorbed 50 c.c.		Nil	

12 minutes' continuous shaking required to bring about complete absorption.

Volume of gas after removal of CO <sub>2</sub> and oxygen.		c.c.
		40·16
Volume after contact with Cu <sub>2</sub> O suspension.	{ ½ minute's shaking. 20 minutes' shaking. 25 minutes' without shaking. 10 minutes' shaking.	39·05
		29·9
		27·55
		23·80

Rate of absorption with shaking, about 4 times that without shaking.  
 Volume absorbed in first ½ minute = 1·1 c.c. (*cf.* 15·25 c.c. with cuprous chloride).  
 About 30 minutes' shaking required for complete absorption.

Volume after removal of CO <sub>2</sub> and oxygen.		c.c.
		37·88
Volume after contact with Cu <sub>2</sub> O suspension.	{ 10 minutes' shaking. 1½ hours' standing, with occasional shaking. 5 minutes' shaking. " " " "	26·6
		20·0
		18·22
		17·80
		17·80

Rate of absorption with shaking, about 3 times that without shaking.

EFFECT OF THE AMOUNT OF PREVIOUSLY ABSORBED CARBON MONOXIDE ON THE EFFICIENCY OF THE THREE ABSORBENTS DESCRIBED.—This effect has been studied quantitatively. In the case of cuprous chloride the average figures from three or four samples of each solution have been taken.

The following table shows the relation between total volume of carbon monoxide previously absorbed by a sample of each solution (column 1) and the volume of carbon monoxide that that sample fails to take up.\*

\* In all cases this residual carbon monoxide was mixed with 15 to 25 c.c. of hydrogen and nitrogen.

Volume of CO previously absorbed by 100 c.c.	Volume of CO left behind (in presence of 20 c.c. neutral gas).		
	by acid cuprous chloride.	by ammoniacal cuprous chloride.	by $\text{Cu}_2\text{O}$ suspension.
c.c.	c.c.	c.c.	c.c.
0	0.3	0.0	0.0
1	0.3	0.0	0.0
3	0.3	0.0	0.0
5	0.4	0.0	0.0
10	0.4	0.0	0.0
15	0.4	0.1	0.0
20	0.5	0.1	0.0
30	0.5	0.1	0.0
40	0.5	0.1	0.0
50	0.6	0.2	0.0
60	0.7	0.2	0.0
80	0.9	0.2	0.0
100	1.0	0.3	0.0
150	1.3	0.4	0.0
200	1.8	0.6	0.0
500	—	—	{ 0.2 0.0

Taking into consideration the experiments on rate of absorption, the poor absorption by old solutions would appear to be an equilibrium effect rather than one due to low rate of absorption. Except in the case of fresh ammoniacal solution, which does not contain more than 0.05 c.c. of dissolved CO per c.c., cuprous chloride does not absorb to completeness.

On the other hand, absorption by the cuprous oxide suspension has shown itself to be complete.

SUMMARY.—(1) The acid solution of cuprous chloride does not, under any circumstances, effect complete absorption of carbon monoxide.

(2) The ammoniacal solution of cuprous chloride, if it has not previously absorbed more than about 5 per cent. of its own volume of carbon monoxide, does effect complete absorption.

(3) Previously absorbed carbon monoxide interferes with the completeness of the absorption in the case of both these solutions.

(4) Cuprous oxide in sulphuric acid containing  $\beta$ -naphthol gives complete absorption of carbon monoxide, even when it has previously absorbed considerable quantities. Its action, however, is slower than those of the chloride solutions.

## PART II.

### Advantages of Using Hot Reagent.

By T. CARLTON SUTTON, M.Sc., F.Inst.P., AND H. R. AMBLER, B.Sc., A.I.C.

Cuprous oxide suspended in a mixture of  $\beta$ -naphthol and sulphuric acid\* is found to absorb carbon monoxide completely. When used in the cold, however, more than ten minutes', and sometimes as much as half an hour's shaking, is needed to secure this result.

\* Lebeau and Bedel (*loc. cit.*).

We find, however, that this defect may be overcome by using the reagent at a temperature of about 60° C. Absorption then takes place within 3 minutes.

The Sodeau apparatus used in the previous work was employed for the analysis. Three and a half metres of 30 S.W.G. Eureka Wire were wound round the lower bulb of the gas pipette and connected with a 20 volt main. This was sufficient to raise the temperature of the bulb and absorbent to about 60° C. and maintain it at that temperature.

After carbon dioxide and free oxygen had been removed, the gas sample was passed into the pipette in the customary way, was duly shaken and, on removal into the jacketed "reading burette," was allowed to stand so as to regain the initial temperature. Thirty seconds were found to be sufficient for this purpose. Some typical absorptions showing the effect of warming and of shaking are given in the following table:

		Burette readings	Per centage of CO absorbed.	Time of shaking required for complete absorption.
		c.c.	c.c.	
Room Temp.	Vol. gas before shaking with absorbent	42.89	0	
	" " after 3 minutes' shaking with absorbent	25.36	76	
15° C. to 20° C.	" " " 6 " " " "	20.12	98.5	12 minutes.
	" " " 9 " " " "	20.06	99.2	
	" " " 12 " " " "	20.01	100	
	" " " 15 " " " "	20.01	100	
	Vol. gas before shaking with absorbent	40.16	0	
	" " after ½ minute's shaking with absorbent	39.05	7	About 30 minutes (contact without shaking not effective).
	" " " 20 " " " "	29.90	63	
	" " " further 25 minutes' contact without shaking	27.55	77	
	" " " " 10 " " shaking	23.80	100	
	" " " " 10 " " "	23.80	100	
	Vol. gas before shaking with absorbent	37.88	0	
	" " after 10 minutes' shaking	26.00	59	At least 15 minutes (contact without shaking not effective).
	" " " additional 1½ hours' standing with occasional shaking	20.00	89	
	" " " further 5 minutes' shaking	18.22	98	
	" " " " 5 " " "	17.80	100	
	" " " " 5 " " "	17.80	100	
Temp. 60° C. to 70° C.	Vol. gas before shaking with absorbent	38.65	0	
	" " after 1 minute's shaking	34.10	31	3 minutes.
	" " " 3 " " "	24.20	99.9	
	" " " 5 " " "	24.18	100	
	" " " 7 " " "	24.18	100	
	Vol. gas before shaking with absorbent	29.30	0	
	" " after ½ minute's shaking	23.10	48	1½ minutes.
	" " " 1½ " " "	16.54	100	
	" " " 2½ " " "	16.54	100	

We have been using this method for some of our routine work and would recommend it for careful consideration to anyone who deals habitually (as we do) with mixures containing, say, carbon dioxide, carbon monoxide, oxygen, nitrogen, hydrogen, and methane.

Our thanks are due to the Director of Artillery for permission to publish this paper.

RESEARCH DEPARTMENT,  
ROYAL ARSENAL, WOOLWICH.

## The Examination of Charred Documents.

BY C. AINSWORTH MITCHELL, M.A., F.I.C.

*(Read at the Meeting, February 4, 1925.)*

THE special difficulties in an examination of documents become incomparably greater when the paper or other groundwork material has been injured by fire, and then it is often only by the most careful manipulation that it is possible to decipher any characters that may be present, or to ascertain the medium in which they were made.

The first scientific investigation of the subject appears to be that made by Sir Humphry Davy (*Phil. Trans. Roy. Soc.*, 1821, 191), when in 1819 he made a series of experiments to discover the best means of dealing with the charred Greek and Roman papyri which had been recovered from the ruins of Herculaneum where for over seventeen hundred years they had lain buried beneath layers of volcanic ash and tufa from Vesuvius. This had excluded the air, and the separate leaves of papyrus had become matted into compact scorched masses into some of which water had permeated, turning them black. Of the various methods of separation tried, that found to be most successful was to saturate the caked masses with chlorine or iodine vapour and then to heat them very gradually so as to expel the gas from between the individual leaves. Finally these were coated on the back with a solution of glue gelatinised by the addition of alcohol. In this way, fragments of a large number of papyri were separated and rendered legible, and it was proved by means of tests with potassium ferrocyanide that the inks upon them were not iron-gall inks.

It is, of course, now well known that all the inks upon early papyri were carbon inks (*cf. Lucas, ANALYST, 1922, 47, 22*), but, had the inks on these Herculaneum MSS. been of the more modern type, they could hardly have escaped being bleached by the action of the chlorine. Davy mentions that he tried carbon dioxide as a separating agent, but did not obtain such good results with it as with chlorine.

RESTORATION OF IRON INKS.—The method of testing for iron in inks by means of ferrocyanide was first used by Blagden in 1787 (*Trans. Roy. Soc.*, 1787, 77, 451) in his experiments to ascertain the nature of the inks on ancient parchments from the ninth century A.D. onwards. On the whole, it gives more satisfactory results than treating the parchment or paper with a decoction of galls, which was described by Canneparius, in 1660, in his book on inks (*De Atramentis*), but a solution of gallic acid is preferable to gall nut extract for restoring writing on parchment MSS. rendered illegible by age or by scorching, and was recently found effective for the purpose by Matthews (*ANALYST*, 1924, 49, 516). In the case of charred or incinerated paper, however, neither ferrocyanide nor gallic acid is satisfactory, since the coherent fabric of char or ash is too porous, and the reagent spreads through the mass, making it so pulpy that it is difficult to handle.

I therefore made experiments with various reagents in the form of vapour. Nitric oxide will sometimes bring out the writing on calcined fragments, evidently through its combination with the ferrous sulphate reduced from the ferric basic sulphate in the burning process. This method is very uncertain, however, and it is much better to use thiocyanic acid vapour (obtained by heating a solution of a thiocyanate with hydrochloric acid). Under favourable conditions the reaction is very effective, a dark iron thiocyanate being formed from the residual iron from a writing. For example, quite illegible writing upon dark brown scorched paper was thus developed in very dark characters.

The reaction is an extremely sensitive one, and in a series of test experiments I have found it capable of detecting as little as 1 part of iron in 300,000. It is not surprising, therefore, that it does not give good results when the paper itself contained much iron.

METHODS OF CALCINING.—It is only in exceptional cases that charred documents can be deciphered without continuing the calcination one or more stages further, and the difficulty I had to overcome was to be able to stop the process at any desired stage of charring, for some characters show up best on a light brown char, others on grey or white ash. The method I ultimately adopted was to place the fragment between two pieces of fine wire gauze and to hold these by means of the crucible tongs in a Bunsen flame. From time to time this gauze holder is withdrawn from the flame and the fragment examined, and in this way not only does the calcination proceed evenly, but the curling up of the edges of the paper is prevented to a large extent.

DIFFERENTIATION OF PIGMENTS BY CALCINATION.—Apart from its use in the development of illegible writing in ink or pencil, or of printed or typewritten characters, this method of calcining can also be used as a means of differentiating different pigments on unburnt paper.

Ordinary writing inks, on ignition, leave a residue probably consisting of a mixture of ferrous and ferric salts, and these show a different appearance on the charred ink according to the amount of iron in the ink. The intensity of the thiocyanic acid reaction may then afford a further means of differentiation.

*Pigments.*—Graphite is very difficult to burn away, even in the form of the thin deposit from a pencil. With moderate ignition a pencil mark is readily developed upon charred paper, and the microscopical appearance of the black line of residual graphite may be very characteristic. For instance, Rowney's indelible black pencil leaves a pale dark grey line on a grey ash from the paper, quite different from that given by the old Borrowdale pencils.

The silver striations due to the silicious impurities in the graphite or in the clay of the pencil, can usually still be clearly discerned in the calcined lines, and enable one to ascertain which of two intersecting lines is uppermost (*cf.* ANALYST, 1922, 47, 386).

*Copying Ink Pencils.*—I have already shown (ANALYST, 1917, 42, 3) that the pigments of these violet pencils can be differentiated on paper by various reactions based on the difference in their composition, and I have given a table showing that their pigments can be grouped into different classes in accordance with their relative contents of graphite, kaolin clay and violet dye.

Those pigments containing a considerable amount of graphite yield a well-defined line of graphite after calcination, whereas those free from graphite may show a white streak (due to alumina) or a grey ash, or, if the calcining is done too rapidly, leave no visible residue. The iron present also influences the result.

The following results are typical of those obtained:

<i>Copying Ink Pencil.</i>		<i>Result obtained.</i>
Eagle Atlas 824 .. ..	..	Grey characters on white ash.
"Atlas" 823 .. ..	..	Ditto.
Faber's .. ..	..	Brick-red characters on grey ash.
Duplex (American Pencil Co.)		Fawn-brown characters.
Hardtmuth's .. ..	..	Greyish graphite streak on white ash.
Hessin's .. ..	..	Black graphite streak on white ash.
Japanese .. ..	..	Dark graphite streak.
Kurz .. ..	..	Black graphite line on white ash.
Swan .. ..	..	White on grey ash, or nothing.

The last result is interesting, for it explains why in the case of *Rex v. Wood* (in which charred fragments of paper were found in the grate of a room where a woman had been murdered) so little of the writing remained legible. I have tested writing done with the "Swan" copying-ink pencil found on the prisoner, and it behaved in exactly the same way. The analysis of the pigment explained the reason of this difference; alumina, but no graphite is present.

Another interesting point about the calcination of writing in copying-ink pencil is that if the pigment contains graphite the test enables one to decide which of two intersecting lines is on top. This is quite impossible with any degree of certainty when examining the pigment when freshly written (see Fig. 1), but on burning away the violet dye the black lead remains and the continuity of the silver striations in the lines becomes apparent, just as in the case of writing in ordinary black-lead pencil (see Fig. 2). These photo-micrographs were made by Mr. T. J. Ward under a magnification of 20 diameters.



*Coloured Pencils.*—The calcination test will frequently distinguish between the pigments of different pencils in writing on paper. In some cases the iron in

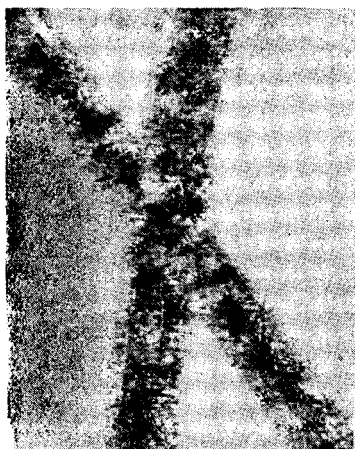


Fig. 1.  
Marks with Copying Ink Pencil,  
× 20.



Fig. 2.  
Marks with Copying Ink Pencil,  
after calcination of paper, × 20.

the pigment is the characteristic ingredient; in others, alumina and occasionally black lead. The following results are typical of those obtained:

<i>Blue Pigments.</i>	<i>Result of Calcination.</i>
American Pencil Co. solid pencil	Dark characters as incrustation completely obliterated to a white ash.
American Duplex copying ..	Faint grey on white ash; barely legible.
Faber's blue copying ..	Faint red on grey ash. Intensified to chocolate brown by HCNS.
Swan Pencil Co. .. ..	White on grey ash.
 <i>Red Pigments.</i>	
Cohen's red pencil ..	White on brown charred paper.
Faber's red pencil ..	White on brown charred paper.
Chamber's red pencil ..	Dark metallic characters on grey ash.
Red solid pencil .. ..	Writing completely obliterated.

The foregoing results are sufficient to prove that the method could be used as a means of identifying these pigments in a given piece of writing, and need only involve the destruction of a word or two of the document.

*TYPEWRITING.*—The earlier typewriting inks, which consisted of an aniline dye mixed with a slowly drying medium, usually containing glycerin, are still in use. As might be expected, they leave no trace of the writing when the paper is calcined, and this distinguishes them from the more modern inks which are more of the nature of printing inks, and contain lampblack, colour lakes, and oil-soluble

dyes. Those containing gasblack or other forms of lampblack can be quite clearly developed by cautious ignition between the wire gauze support, but if the heating is continued too long the carbon soon burns away. Typewriting inks containing coloured lakes may also leave a characteristic residue.

PRINTING INKS.—Black printing inks, which contain lampblack or gasblack, behave like the analogous typing inks. This form of amorphous carbon is not completely burned away in a short time until the temperature reaches 305°–310°, and as the carbonised paper is burned away long before that temperature is reached, it is quite a simple matter to develop printed characters on a white ash if the calcination is carefully followed.

Blue inks containing Prussian blue may leave a red residue due to the iron present, and this can be intensified by means of thiocyanic acid vapour.

Red printing inks, which frequently contain an organic pigment in the form of a lake, may also give very characteristic results. The organic pigment, of course, burns away, but the alumina may be left as a brilliant white deposit on the black char of the paper. Other red printing inks, containing an iron pigment, leave a brown deposit on a grey ash, and pure vermilion ink leaves black characters on a dark grey ash.

*Illustrative Case.*—The difficulty of the possibility of deciphering printed matter on a charred paper was of primary importance in a case in which I was consulted three years ago. A cashier was charged with appropriating a large sum of money in bank notes that had been entrusted to him. His defence was that in clearing away a pile of waste papers he had accidentally burned the pile of notes, but his story was not accepted, and he was sentenced to a term of imprisonment. He appealed, and asked that the ashes of his bonfire, which he had kept, might be searched. When I examined these ashes I found that less than 20 per cent. consisted of large charred fragments exceeding a half square inch in area, and less than 25 per cent. of still smaller fragments, the remainder being composed of dust and office débris. I estimated the number of large fragments at over 30,000.

It was necessary to examine these individually by oblique light, and, when there was the slightest indication of pattern, the selected fragments were examined more closely, frequently by calcination. By this means about ten fragments showing patterns which could be recognised as forming portions of bank notes could be identified, and ultimately I discovered one fairly large piece upon which the head in the medallion of a note could be unmistakably recognised.

Most of the fragments in the heap on which printed characters could be deciphered were on highly clayed paper. The larger fragments contained nearly 35 per cent. of mineral matter, and the smaller about 28 per cent. The paper upon which Bank of England notes are printed yielded a non-coherent residue containing 8.08 per cent. of mineral matter. These differences were quite sufficient to account for the difficulty of discovering only a few fragments of bank notes, although a bundle had been burned. The only reason why any portions at all of them were found was that they had been calcined in a compact mass, so that the inner portions would be more protected from the flame and thus leave a more

coherent ash. This was proved by experiments with the bank note paper. This evidence in conjunction with the production of fragments of actual charred notes convinced the Appeal Court, and the sentence on the accused was quashed.

**STRENGTHENING AGENTS.**—The case described also shows the difficulty that may be experienced in calcining paper poor in mineral matter. The charred remains of ordinary magazine paper and the like, being heavily loaded with clay, can be developed at once, for it forms an excellent background for printed or written characters. But when only a small amount of mineral matter is present, it is essential to supply it by treating the partly charred fragments with a solution of a suitable salt, and then drying it before calcination. A 10 per cent. solution of aluminium acetate gives very good results; so does a solution of thorium acetate of the same strength. Habermann (*Zeitsch. anal. Chem.*, 1909, **48**, 729) expressed the view that thorium nitrate was unsuitable for this purpose, owing to there being some risk of its oxidising the graphite of lead pencil marks. In view of the difficulty of burning graphite away, I applied tests to ascertain whether such oxidation actually would happen, and I have to thank the Welsbach Light Company for kindly sending me specimens of pure thorium nitrate solution (20 per cent.) and of pure cerium nitrate as used in the preparation of incandescent gas mantles. I found that charred fragments of paper poor in mineral matter leave a compact coherent ash after treatment with thorium nitrate, and that graphite pencil marks are not removed during the calcination. Cerium nitrate, on the other hand, is of little use for the purpose, for it disintegrates the ash fabric into small irregular fragments.

The simplest method of preserving the calcined fragments is to attach the underside to a microscope slide by means of a thin film of seccotine or, if both sides are wanted for examination, the fragments may be sprayed on each side with a transparent spirit varnish and preserved between two pieces of tracing paper.

**PHOTOGRAPHIC METHODS.**—It is frequently possible to decipher dark charred fragments by direct photography with oblique lighting, which often reveals more than can be seen by the eye. According to Dennstedt and Voigtländer (*Lehrbuch der gerichtlichen Chemie*, 1906, p. 120) light grey characters on black backgrounds of char may be brought out well by the use of a red filter and colour-sensitive plate with oblique lighting.

About two years ago an official method of deciphering charred documents by means of photography was published in the United States (Davis, *U.S. Bureau of Standards Sci. Papers*, 1922, **18**, (454), 445; *Abstr. Analyst*, 1923, **48**, 241). This is based upon the principle that a sensitised plate, when left in close contact with a charred fragment of paper, is acted upon by some of the products of the combustion, but that those parts of the plate in contact with any latent writing or printing will be protected from this action. Although the method is a very slow one, at least a week, and often a month, being required to obtain a record of any characters present, it might be useful under certain conditions when calcination is not permissible. Unfortunately my experiments, and those of Mr. T. J. Ward, have shown

that one cannot be certain of getting a successful result however long the exposure is continued. Very much depends upon the degree of charring to which the paper has been subjected. For example, in two typical instances pieces of the same paper with characters in the same printing ink were charred for different periods, then left in close contact with Ilford Rapid Plates for three weeks. The one more lightly charred gave a faint indication of the printed characters, whereas the second piece showed an outline of the paper, but no suggestion of the letters.

Many years ago Dr. Russell showed that ordinary printed matter might record itself on a photographic plate, probably on account of certain peroxides formed by the driers in the printing ink. But the results are just as capricious as with charred fragments. For example, Mr. T. J. Ward obtained an excellent contact reproduction of a fragment of a newspaper within a week, whereas I left portions of another periodical in contact with an Ilford Rapid Plate for a period of five weeks without obtaining any indication of characters on the plate.

My experiments with the charred printed matter were made immediately after the charring, but, as the author of this photographic method points out, its success largely depends upon the contact with the sensitive plate being made as soon as possible. The poor results that I obtained under the most favourable conditions, for I made ten exposures for varying periods of time and only twice obtained a poor record of the printed characters, show that the method, though interesting, is obviously too limited in its application to be of much practical use.

I wish to thank Mr. W. B. Murdoch for specimens of printing in different kinds of ink, and Mr. T. J. Ward for his assistance in the photographic work.

## Notes.

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

### THE FAT OF GOATS' BUTTER.

REFERRING to Mr. Richmond's note (*ANALYST*, 1925, 62), we would repeat that the argument in our paper (*ANALYST*, 1924, 49, 509) was based on the fact that we knew of cases where goat's butter had been sold as "butter."

Whether or not goats' butter is legally butter is a point which is somewhat obscure, although we ourselves incline to the view that, as the law stands at present, it may be described as "butter."

It was with the object of directing attention to the present somewhat unsatisfactory legal position of this product that our notes were mainly written, as a perusal of our conclusions will show.

Mr. Richmond's next point is, "that by the use of accepted methods and especially by the use of formulæ," of which he is the author, we have formed the

conclusion that goats' butter might be condemned as adulterated with coconut oil. (We presume that he has understood our meaning, *viz.* if the sample were received by an analyst as "butter.")

Mr. Richmond is quite correct in assuming that we used one of his formulæ in the manner he indicates. We were astonished, however, to find that a different meaning existed from the one we attributed to the words defining P' in the formula which he gives on p. 249 of *Dairy Chemistry*, 3rd Edition. Doubtless Mr. Richmond was equally surprised. A correct quotation of the formula and directions for its use, both as regards wording and punctuation, taken from that page of his book is:

"Should the Polenske figure exceed the maximum given in the table the quantity of coconut oil present may be deduced from the formula

$$C = \frac{P - P'}{14.4} \times 100.$$

C = percentage of coconut oil.

P = Polenske figure.

P' = mean Polenske figure from the table for a figure equal to the Reichert-Wollny figure found + half the Polenske figure."

Expressed algebraically, we consider that the obvious meaning of Mr. Richmond's words is that  $P' = \phi(a) + b$ , whereas actually they are intended to mean  $P' = \phi(a + b)$ , where the symbol  $\phi$  represents "function."

We fail to see how the unintentional omission of the words "for a figure" affects the meaning of the directions in any way, and in any case our interpretation of the meaning of the words was made before the misquotation complained of.

Incidentally, in his remarks Mr. Richmond also misquotes his book, as the word we have put in italics does not appear therein, *viz.* "calculated for a figure."

However, we frankly admit that we did not use this formula in the manner in which Mr. Richmond now makes clear it should be applied, and we thank him for calling our attention to the mistake.

Naturally the correct use of the formula calls for a modification of the view we had expressed, *viz.* that samples of goats' butter received by an analyst as "butter" might be regarded as cows' butter and coconut oil, as the calculated Reichert-Wollny figures for the apparent original butter would be too high in a great many cases for this to be possible.

Further, it still demonstrates what we have already stated—that the formula cannot be made to apply to goats' butter. We are well aware that it was not designed to do so, but we have endeavoured to place ourselves in the position of an analyst who received such samples as "butter." In the case of certain mixtures of goats' and cows' butter, which might be described as "butter," we still maintain that, although other determinations might lead to a contrary view, the inference from the Reichert-Wollny, Polenske and Kirschner figures is that coconut oil had been added, and therefore so far as such "butters" are concerned, these figures are unreliable. This can be seen from the figures these determinations would give if applied to "butters" made by blending the following percentages of our average goats' butter with average cows' butter. This has been verified by experiment.

The average of our results for goats' butter would give:—R.W., 26.44; P., 7.3; K., 18.

The average for cows' butter is taken as:—R.W., 28.4; P., 2.3; K., 24.

From mixtures of these, approximately the following figures would be obtained on analysis:

	<i>Percentage of Goats' Butter.</i>			
	20	30	40	50
R.W. No.	28.01	27.81	27.62	27.42
P. No.	3.30	3.80	4.3	4.8
K. No.	22.8	22.2	21.6	21

Application of the coconut oil formula to these figures would indicate the following:

	<i>Percentage of Coconut Oil indicated.</i>			
	3.82	7.15	10.63	14.1

Calculating the Reichert-Wollny figure of the apparent original butter from these figures would not arouse suspicion, but, of course, with higher percentages of goats' butter high calculated Reichert-Wollny figures would be obtained. For the above mixtures the figures are:

R.W. of apparent coconut oil	..	..	0.3	0.57	0.85	1.13
R.W. apparently due to butter portion	..	27.70	27.24	26.77	26.77	26.29
Calculated R.W. of original butter	..	28.80	29.34	29.95	30.61	

With goats' butter of as low Reichert-Wollny value as those recorded by Trimen, the apparent percentage of coconut oil could, of course, be higher.

It appears to us that a person prosecuted for selling a coconut oil butter mixture might offer the defence that it was cows' and goats' butter, and, as such, was entitled to be called "butter."

In conclusion, may we say that our experience leads us to believe that goats' butter is not such a "rare commercial article" as Mr. Richmond states in his letter.

FRANK KNOWLES.  
JOHN C. URQUHART.

### BELLIER'S MODIFIED TEST FOR ARACHIS OIL.

I SHOULD like to direct the attention of other analysts to the fact that imported olive oil is now frequently condemned as containing 5 per cent. of arachis oil, owing to its having given a positive result in a rapid modification of Bellier's test. This modification consists in adding to the saponified oil 1.5 c.c. of Adler's acetic acid solution and omitting the hydrochloric acid from the alcohol. Under these conditions the test sometimes gives a cloudiness at or about 16° C. By the use of Luer's modification, however, in which 3 drops of glacial acetic acid are added to the saponified product (ANALYST, 1913, 38, 58) no turbidity results. In my experience a cloudiness or precipitate at 17° C. is indicative of the presence of arachis oil, but it is unsafe to base judgment on a turbidity at 16° C.

As this supposed detection of arachis oil is causing great loss to the sellers of olive oil, I should be glad to know the experience of other analysts as to the degree of accuracy of this modification of the test.

F. F. SHELLEY.

## PREPARATION OF NESSLER'S SOLUTION.

THE note under the above title by Mr. H. Droop Richmond in the February issue reiterates a statement that is commonly encountered in the literature of water analysis, namely, that "The sensitiveness of Nessler's solution . . . usually increases with age." My own experience is quite at variance with this statement, and since reading it I have made a test, the method and results of which are sufficiently set out in the table below, to determine whether ageing had the effect alleged.

Nessler's solution.	2 c.c. of the solution added to 50 c.c. of water:		
	Containing 0.01 mgrm. $\text{NH}_3$	Containing 0.003 mgrm. $\text{NH}_3$	Ammonia-free and used to prepare fore- going standards.
1. 14 years old; stored in 2 c.c. sealed glass ampoules.	Distinct coloration, but less than No. 2.	Coloration just discernible.	No coloration.
2. 6 months old; stored in stock bottle.	Distinct coloration, but less than No. 4.	Coloration quite definite.	No coloration.
3. 3 days old; from stock bottle.	Same as No. 2.	Same as No. 2.	No coloration.
4. 6 months old; from stock bottle and sensitised immediately before use.	Very distinct coloration.	Coloration marked and distinctly more than No. 2.	No coloration.

These observations were confirmed by an assistant who had no knowledge of the contents of the glasses. It is submitted that the tests show the statement to be inaccurate. The process of sensitising the Nessler solution, as is well known, consists in adding, to a suitable quantity withdrawn from the stock bottle, saturated mercuric chloride solution, drop by drop, with shaking, until a distinct yellow turbidity is produced, but it is not usually known that the effect remains at a maximum for only about 2 hours; this turbidity and coloration disappears when 2 c.c. of the solution are added to the 50 c.c. of water usually tested. It may be noted that the difference in colour intensity produced by a sensitive and an insensitive Nessler solution is much more marked when a quantity of ammonia of the order of 0.005 mgrm. is present than with larger amounts.

ROBERT C. FREDERICK.

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## DYED ORANGES.

WHAT appears to be a fresh example of ingenuity in colouring food to make it more attractive to the eye has recently been met with by the writer. Some oranges, which appeared to be ripe, were examined, and the redness of their skins was found to be due to artificial colour. A sample of the colouring matter said to be used for this purpose was proved to be a solution of chrysoidine, which, it may be mentioned incidentally, is also used for making bait appear more alluring to fish.

A point of distinction between dyed and natural oranges is that the calyx of the former is red, that of the latter green. On boiling the peel with water containing 10 per cent. of potassium bisulphite and a fragment of woollen fabric (nun's veiling) the fibres are coloured pale yellow in the case of natural oranges, and deep yellow with dyed oranges.

J. F. LIVERSEGE.

## Notes from the Reports of Public Analysts.

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

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### CITY OF BIRMINGHAM.

#### REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1924.

DURING the fourth quarter of last year 1320 samples were submitted for analysis, of which 1118 were analysed under the Sale of Food and Drugs Acts. Of the food and drugs samples, 955 were bought informally (12 adulterated), and 163 were bought under the provisions of the Acts (9 adulterated).

**MILK.**—Of the 604 samples examined, 11 contained less than 11·5 per cent. of total solids. The percentage of adulteration was 1·8.

**BUTTER.**—One of 84 informal samples contained 19·5 per cent. of water. A subsequent formal sample contained only 13·9 per cent.

**MARGARINE.**—One of 106 informal samples was adulterated with boric acid (0·7 per cent.). Two formal samples bought as "Margarine mixed with Butter" contained less than 1 per cent. of butter. The vendor was cautioned.

**JAM, JELLY.**—Eight informal samples were free from boric or salicylic acid. One sample each of apricot, damson and raspberry jam contained glucose syrup, and two of them were labelled "made from refined sugar." The vendors were cautioned for the false labels.

**PLANT AND VEGETABLE MANURES.**—Eight samples were examined for the Agricultural and Small Holdings Committee. One contained excess of insoluble phosphates (17·48 per cent. guaranteed, 23·3 per cent. found).

**MIXED POULTRY CORN.**—One of 4 samples examined was composed of 33 per cent. of flint grit, 34 per cent. of maize, 32 per cent. of rye, and 1 per cent. of wheat. The vendor was cautioned, and a circular was sent by the Town Clerk to corn dealers in the city, pointing out that grit is not corn, and that "mixed corn" must consist of corn.

J. F. LIVERSEEGE.

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## Legal Notes.

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

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### EXCESS OF QUININE IN PRESCRIBED MEDICINE.

ON February 6 the proprietors of a drug store were summoned before the Islington Justices on the charge of supplying a medicine not in accordance with the purchaser's demand.

A prescription had been handed to the defendant requiring, among other ingredients, 2 grains of quinine sulphate in each half-ounce. The medicine was supplied and, on analysis, was found to contain an excess of 25 per cent. of quinine sulphate.



For the defence it was pointed out that there could be no intent to defraud in this case. The directors of the stores had made inquiries and had found that the quinine sulphate used had lost almost all its water of crystallisation. The result was that the medicine was found to contain more quinine sulphate (in terms of the B.P. article) than the amount of drug that was, in fact, put in. This was not put forward as an answer in law to the charge, but as grounds for mitigation.

A fine of £5 with £2 2s. costs, was imposed.

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### TURPENTINE SUBSTITUTE.

ON February 27th a tradesman was summoned under the Food and Drugs Acts by the Shoreditch Borough Council, for having sold as "turpentine" an article that consisted entirely of petroleum derivatives.

The defendant pleaded ignorance of the matter.

Evidence was given by the inspector that on his instruction a boy was told to buy two pennyworth of turpentine. The boy had previously bought some for his mother. The mother of the boy stated that the "turpentine" previously bought had blistered her skin.

The defendant stated that he did not know what effect the contents of the bottle would have on the skin. He only knew that many children asked for "turps" without any definition, and others for "best turps."

Mr. Ray said that the defendant kept an oil shop, and that it was a general custom for the public to buy household remedies from such shops. The prosecution contended that if these shops sold things that were for use medicinally, they should not be allowed to claim that they were not subject to the Food and Drugs Acts. Turpentine undoubtedly came within the definition of a drug.

The Magistrate (Mr. Clarke Hall) pointed out that the defendant had admitted that it was his practice to sell this stuff unless the best turpentine was asked for. It was entirely a false description. Poor people came to him, and he sold them a substance that did them injury. Defendant must pay £20, which was the maximum penalty that the law allowed.

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### CIDER VINEGAR FROM DRIED APPLES.

#### U.S.A. SUPREME COURT DECISION.\*

IN 1920 it was decided in an Ohio Court that 95 barrels of alleged apple cider vinegar sent by a New York company into the State of Ohio were adulterated and misbranded, for the reason that vinegar made from evaporated or dried apple products had been mixed and packed with and substituted wholly or in part for apple cider vinegar.

In 1922 the shippers appealed to the Circuit Court of Appeal on writ of error, and the judgment of the lower Court was reversed. The U.S.A. Government then appealed to the U.S. Supreme Court.

The facts not in dispute were that the claimants made apple cider and apple cider vinegar from fresh apples during the apple season from about September 25 to December 15, and during the remainder of the year they made these products from evaporated apples. In the evaporation process sulphur fumes were applied

\* U.S.A. Dept. Agriculture, Service and Regulatory Announcements, No. 12367, pp. 194-205.

to prevent rot and discoloration, and about 80 per cent. of the water was removed by evaporation. In using the product for the preparation of cider vinegar, an amount of pure water substantially equivalent to that removed was added, and the sulphur was removed by the addition of barium carbonate. The traces of barium left in the extract did not constitute adulteration within the meaning of either of the paragraphs of Sec. 7 of the U.S. Food and Drugs Act, and were not alleged by the prosecution to be injurious or deleterious.

After being submitted to alcoholic and acetic fermentations the aqueous extract of the dried apples gave chemical results similar to those obtained from an analysis of cider vinegar from fresh apples, except that it contained the above-mentioned traces of barium.

After reviewing these facts the Supreme Court, in its judgment, cites the provisions of Sec. 6 of the U.S.A. Food and Drugs Act on labelling, and proceeds as follows:

"The statute is plain and direct. Its comprehensive terms condemn every statement, design, and device which may mislead or deceive. Deception may result from the use of statements not technically false or which may be literally true. The aim of the statute is to prevent that resulting from indirection and ambiguity, as well as from statements which are false. It is not difficult to choose statements, designs, and devices which will not deceive. Those which are ambiguous and liable to mislead should be read favourably to the accomplishment of the purpose of the Act. The statute applies to food, and the ingredients and substances contained therein. It was enacted to enable purchasers to buy food for what it really is. (*United States v. Schider*, 246 U.S. 519, 522; *United States v. Lexington Mill Co.*, 232 U.S. 399, 409; *United States v. Antikamnia Co.*, 231 U.S. 654, 665.)

"The vinegar made from dried apples was not the same as that which would have been produced from the apples without dehydration. The dehydration took from them about 80 per cent. of their water content—an amount in excess of two-thirds of the total of their constituent elements. The substance removed was a part of their juice from which cider and vinegar would have been made if the apples had been used in their natural state. That element was not replaced. The substance extracted from dried apples is different from the pressed-out juice of apples. Samples of cider fermented and unfermented made from fresh and evaporated apples, and vinegar made from both kinds of cider were submitted to and examined by the District Judge who tried the case. He found that there were slight differences in appearance and taste, but that all had the appearance and taste of cider and vinegar. While the vinegar in question made from dried apples was like, or similar to that which would have been produced by the use of fresh apples, it was not the identical product. The added water, constituting an element amounting to more than one-half of the total of all ingredients of the vinegar, never was a constituent element or part of the apples. The use of dried apples necessarily results in a different product.

"If an article is not the identical thing that the brand indicates it to be, it is misbranded. The vinegar in question was not the identical thing that the statement, 'Excelsior Brand Apple Cider Vinegar made from selected apples,' indicated it to be. These words are to be considered in view of the admitted facts and others of which the court may take judicial notice. The words 'Excelsior Brand,' calculated to give the impression of superiority, may be put to one side as not liable to mislead. But the words, 'apple cider vinegar made from selected apples,' are misleading. Apple cider vinegar is made from apple cider. Cider is the expressed juice of apples, and is so popularly and generally known. It was stipulated that the juice of unevaporated apples when subjected to alcoholic and

subsequent fermentation is entitled to the name 'apple cider vinegar.' The vinegar in question was not the same as if made from apples without dehydration. The name 'apple cider vinegar' included in the brand did not represent the article to be what it really was; and, in effect, did represent it to be what it was not—vinegar made from fresh or unevaporated apples. The words 'made from selected apples,' indicate that the apples used were chosen with special regard to their fitness for the purpose of making apple cider vinegar. They give no hint that the vinegar was made from dried apples, or that the larger part of the moisture content of the apples was eliminated and water substituted therefor. As used on the label, they aid the misrepresentation made by the words 'apple cider vinegar.'

"The misrepresentation was in respect of the vinegar itself, and did not relate to the method of production merely. When considered independently of the product, the method of manufacture is not material. The act requires no disclosure concerning it. And it makes no difference whether vinegar made from dried apples is or is not inferior to apple cider vinegar.

"The label was misleading as to the vinegar, its substances, and ingredients. The facts admitted sustain the charge of misbranding.

"Judgment reversed."

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## Department of Scientific and Industrial Research.

### FOOD INVESTIGATION BOARD.

#### Special Report No. 21.

#### THE "GAS" CONTENT AND VENTILATION OF REFRIGERATED HOLDS CARRYING APPLES.\*

In a ship's hold carrying fruit the atmospheric conditions are influenced by the respiration of the fruit and by leakages from the hold, either by mass movement or by diffusion. The results of daily measurements of the carbon dioxide and oxygen concentrations in two "unventilated" holds during a voyage from Australia showed that the carbon dioxide concentration rose rapidly until more or less steady values were obtained, and remained steady until another rise occurred towards the end of the voyage, the oxygen concentration showing inverse changes. Assuming the leakage to be entirely by mass movement, a daily exchange of at least 10,000 cb.ft. per day between the atmospheres inside and outside the hold must have taken place. Effects of ventilation are only temporary. The observed value of the sum of the carbon dioxide and oxygen concentrations in the hold (21.0 for ordinary air) remained practically steady throughout the voyage in the two holds examined, and was between 21.3 and 21.6, due either to the respiratory quotient being greater than 1, and/or to leakage by diffusion of oxygen in at a greater rate than of carbon dioxide out. During the last few days of the voyage the (CO<sub>2</sub>+O<sub>2</sub>) value fell in one hold (data not available for the second). Carbon dioxide production had then increased, and must have been accompanied either by a still more rapid increase of oxygen consumption, or a decreased rate of leakage by diffusion (not by mass movement).

D.G. H.

\* Obtainable from Adrastal House, Kingsway, W.C. Price 1s. 3d. net.

## Special Report No. 22.

## "BROWN HEART IN AUSTRALIAN APPLE SHIPMENTS."\*

THE accumulated data point conclusively to the appearance of brown heart being due to the accumulation of carbon dioxide in the presence of a certain amount of oxygen in the ship's hold. In observations made in two ships' holds the safety limit of 10 per cent. of carbon dioxide was reached at the end of the first fortnight, and in holds showing high percentages of carbon dioxide (over 15 per cent.) the apples have invariably been found to be diseased. Moreover, in 10 common Australian varieties of apples brown heart has been induced by restricted ventilation at the temperature of ships' holds, the extent of disease increasing with the rising carbon dioxide percentage. Orchard conditions and factors inherent to the fruit, and its degree of maturity, may govern susceptibility to the disease. When apples are stored in holds, as noted in Report No. 21, the proportion of carbon dioxide produced rises steadily, reaches a level, and then, after a considerable steady interval, rises again. This phenomenon can be reproduced in sealed boxes of apples, and in the case of 150 lbs. of fruit thus stored, and maintained at an even temperature of 34-38° F., the percentage of carbon dioxide rose to 23-25 per cent., remained steady for 18 days, and rose again at the rate of 0.5 per cent. per day for 40 days until conclusion of the experiment. This would appear to be the result of the setting up of pathological conditions in the fruit, bringing about increased rate of carbon dioxide production. Experiments are being carried out to determine definitely whether the occurrence of brown heart is accompanied by increased rate of carbon dioxide production.

D. G. H.

\* Obtainable from Adrastal House, Kingsway, W.C.2. Price 1s. 3d. net.

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## Dangerous Drugs Convention.\*

THE International Drugs Convention, which will come into force when ratified, contains the following enactments:—

*Medicinal opium* means raw opium, powdered, granulated or mixed with indifferent materials, dried at 60° C., and containing less than 10 per cent. of morphine.

*Morphine, cocaine, ecgonine* and *diacetylmorphine* are defined as the substances represented by their chemical formulæ, and *Indian hemp* means the dried flowering or fruiting tops of the pistillate plant, *Cannabis sativa* L., from which the resin has not been extracted, by whatever name they may be called in commerce.

Raw opium, coca leaves and other dangerous drugs, including all official and non-official preparations, such as anti-opium remedies, containing more than 0.2 per cent. of morphine and 0.1 per cent. of cocaine, or any alkaloid of opium or coca leaf, are only to be produced, distributed, imported and exported for medicinal and scientific purposes, and, to ensure this, the contracting parties are to exercise due control. Accurate records of manufacture by licensed persons are to be kept. Emergency supplies to the public, by pharmacists, of preparations containing a maximum of 25 mgrms. of opium are allowable at the discretion of the contracting nation.

D. G. H.

\* *Pharm J.*, 1925, **114**, 226-227.

## Italian Regulations on Colouring Matters.\*

REVISED regulations for the use of colouring matters for non-textile purposes came into force in Italy on January 1, 1925, by a Royal Decree.

Colours containing arsenic, antimony and several other compounds may not be used in the preparation of food or for colouring paper in which food is to be packed, or for colouring containers for storing foods or beverages. These pigments may not be used for dentifrices or for colouring toys, but certain compounds of lead, antimony, barium, tin and zinc are allowable for toys. The use of colours containing arsenic, antimony, chromium, tin, zinc, uranium, and cyanogen derivatives is prohibited in soap, except in the case of certain medicated soaps. Arsenical pigments may not be used for colouring fabrics for upholstery, clothes, tapestry, artificial flowers, fruits or leaves, or for wall paper, candles, stationery, lamp-shades, etc.

Cosmetics, dyes and other preparations for colouring the skin must have the name of the manufacturer or seller on the package. If they contain poisonous substances, such as compounds of lead, silver or copper, or paraphenylenediamine, pyrogallol, aminophenol and the like, the exact nature of the contents must be printed on the label, and a yellow band must be attached on which is printed, in characters at least 4 mm. high, an intimation that the contents of the package may be injurious.

\* The Decree (in Italian) may be seen at the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

## The Institute of Chemistry.

FORTY-SEVENTH ANNUAL GENERAL MEETING, 2ND MARCH, 1925.

THE President (Prof. G. G. Henderson), after referring to the loss sustained by British Chemistry by the death of Sir George Beilby, one of the Past Presidents, announced that the Council had invited the co-operation of the Society of Chemical Industry and the Institute of Metals, of which Sir George had also been President, in establishing some fitting memorial in his honour. Prof. Henderson also paid a high tribute to Sir James Dobbie, Government Chemist, to Mr. Otto Hehner, who had achieved a world-wide reputation for his investigations in the chemistry of food and drugs, and to Prof. G. D. Liveing, who had laid the foundations for the great school of chemistry, which had since been developed by Sir William Pope at Cambridge.

At the conclusion of the formal business, the President, supported by Prof. Thomson, made a presentation, on behalf of the Fellows and Associates, to Mr. Richard B. Pilcher on completing thirty years as Secretary and twenty-five years as Registrar and Secretary of the Institute. In the evening, the Council entertained Mr. and Mrs. Pilcher and their family to dinner at the Hotel Russell, followed by a reception.

The Officers and Council for the year ending March, 1926, were elected as follows:—

*President.*—George Gerald Henderson.

*Vice-Presidents.*—Edward Charles Cyril Baly, Edward Richards Bolton, Alfred Chaston Chapman, Thomas Slater Price, Arthur Smithells, and Edward William Voelcker.

*Hon. Treasurer.*—Patrick Henry Kirkaldy.

*General Members of Council.*—Leonard Archbutt, Francis William Frederick Arnaud, Hugh Charles Loudon Bloxam, Arthur Jenner Chapman, Frederick Daniel Chattaway, Harold Govett Colman, William Murdoch Cumming, Alfred Vincent Elsdon, Thomas Gray, Richard Henry Greaves, Arthur James Hale, Isidor Morris Heilbron, William Henry Lewis, Thomas Macara, Hamilton McCombie, Robert Selby Morrell, Robert Howson Pickard, Benjamin Dawson Porritt, Frank Lee Pyman, William Rintoul, William Henry Roberts, William David Rogers, Fred Scholefield, Harry Silvester, Arthur Slator, Jocelyn Field Thorpe, and James Fowler Tocher.

*Censors.*—Alfred Chaston Chapman, Sir Herbert Jackson, Gilbert Thomas Morgan, and Sir Robert Robertson.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

### Food and Drugs Analysis.

**Detection of Putrefying Flesh by means of Alcohol.** Lüttge and Mertz. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 48, 451-452.)—Amino acids are a constant decomposition product of flesh, and these finally yield ammonia and carbon dioxide. If, therefore, the amount of ammonia liberated on treatment with sodium hydroxide is high, it is indicative of putrefaction. The method is to extract with alcohol, which coagulates the albumin and dissolves the amino acids, which may be identified or determined. From 0.5 to 0.8 gm. is treated with 10 c.c. of alcohol and tested qualitatively for amino acids by the addition of a 1 per cent. alcoholic solution of ninhydrin or with  $\alpha$ -naphthylisocyanide or, quantitatively, by the Sørensen titration or the micro-Kjeldahl method. Any considerable amount of amino nitrogen indicated by these tests shows decomposition.  
H. E. C.

**Determination of Maltose in the Presence of Glucose.** M. P. Nottin. (*Bull. de l'Assoc. des Chim.*, 1924-25; 44, 143-145; *J. Inst. Brew.*, 1925, 31, 145.)—The method depends upon the fact that maltose reduces Barfoed's solution to a small but definite extent. In the case of solutions of a concentration of 1 per cent. this reducing power of maltose was found to be 0.07 in terms of glucose as unity. Since the corresponding value with Fehling's solution is 0.572, the ratio of maltose to glucose in a solution containing not more than 0.5 per cent. of the reducing sugar (in terms of glucose) can be calculated from the results obtained with the two reagents the results of determinations by this method agreed with those found polarimetrically, and by fermentation with a yeast that does not ferment maltose.

**The Dextrose and Fructose Ratio in Honey.** A. Gronover and E. Wohnlich. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 48, 406-411.)—Investigation has been made of the methods and conclusions of Auerbach and Bodlander (*ANALYST*, 1924, 49, 389), who, determining dextrose iodimetrically and fructose by difference, state that the ratio of dextrose to fructose in genuine honey is never less than 100:106. The method is generally accurate, and the results on known mixtures are satisfactory, the accuracy of the process being limited to about 1 per cent. of dextrose, but these authors do not confirm the limiting ratio given by Auerbach and Bodlander. With 33 honeys known to be genuine, the ratio was less than 106 in 16, and in 7 less than 100. None of these samples gave a positive result in Fiehe's reaction.  
H. E. C.

**Non-volatile Acids of the Blackberry.** E. K. Nelson. (*J. Amer. Chem. Soc.*, 1924, 47, 568-572.)—Optically active iso-citric acid constitutes about five-sixths of the total acids of the blackberry, which contains also an appreciable proportion of *l*-malic acid and traces of oxalic, succinic, and citric acids.  
T. H. P.

**Reducing Substances in Different Vinegars.** G. Reif. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 48, 424-435.)—The purity of artificial acetic acid, whether prepared from acetylene or from wood distillation, can be judged by its reducing action on permanganate. This action is particularly due, in the case of acid prepared from acetylene, to traces of toxic compounds, such as crotonaldehyde and crotonic acid. If 1 c.c. of a 1 per cent. solution of permanganate be added to 5 c.c. of the acid diluted with 15 c.c. of water, crude wood acid (9.6 per cent.) decolorises the permanganate instantly; technically pure (50 per cent.) acid only after a few minutes; and chemically pure acid remains pink for 15 minutes. The action on permanganate of a large number of compounds when added in quantities ranging from 0.005 grm. to 0.2 grm. per 5 c.c. is tabulated, the most important reducing substances being crotonic acid and the cresols; butyric and oxybutyric acids, furfural and acetone, also reduce fairly rapidly. In wine vinegar the reducing substance is acetyl-methyl-carbinol, which substance also occurs in apple, raspberry and malt vinegars. Its detection, by Farnsteiner's method, serves for the differentiation of wine vinegar from spirit vinegars, or for the detection of wine vinegar in vinegar essences.

*Note.*—Farnsteiner (*Zeits. Unters. Nahr. Genussm.*, 1899, 2, 198) distils 50 c.c. of vinegar, collecting 10 c.c. which is neutralised, mixed with 10 c.c. of Fehling's solution, and allowed to stand at the ordinary temperature. Spirit vinegars show no change of colour, but wine vinegars give a green coloration in about an hour, followed by deposition of copper oxide.  
H. E. C.

**The Fatty Acid Constituents of some Natural Fats. I. The Oils from the Coconut.** E. F. Armstrong, J. Allan and C. W. Moore. (*J. Soc. Chem. Ind.*, 1925, 44, 63-68T.)—A series of fractions was obtained of which every alternate member is claimed to consist of a pure ester, and thus allowed of its identity

being definitely established, so that there was no assumption in the identification of the middle fractions. The preliminary treatment and separation of the fatty acids before esterification depends on their iodine values, and esterification is carried out as follows:—Five hundred grms. of fatty acids are dissolved in 1500 grms. of absolute alcohol, and 150 grms. of concentrated sulphuric acid added (100 grms. in the case of liquid fatty acids). After being boiled for 3 hours the mixture is cooled, the supernatant layer of esters separated, the alcoholic liquor concentrated to about half its bulk, cooled, poured into water, and the esters extracted with petroleum spirit, those previously extracted being afterwards added. The solution is washed with water, mineral acid, and sodium hydroxide solution to remove free fatty acids (which should be recovered, esterified and united to the bulk). The solvent is then removed, and the ethyl esters distilled under reduced pressure, and subsequently fractionally distilled, still under reduced pressure. Reference should be made to the original paper for details of the fractions obtained and their examination. The composition of the coconut kernel oil (from an average sample of the meat of 200 African coconuts with the rind removed) and that of the "parings" oil, *i.e.* oil from the rind, were deduced as follows:

	Caprylic acid.	Capric acid.	Lauric acid.	Myristic acid.	Palmitic acid.	Stearic acid.	Oleic acid.	Linolic acid.
"Parings" oil, per cent.	2(?)	2	28	22	12	1(?)	23	10
"Kernel" oil, per cent.	9.5	4.5	51.0	18.5	7.5	3.0(?)	5.0	1.0

The evidence for the presence of acids of lower carbon content than caprylic acid, even after fractional distillation of the barium salts, was small. D. G. H.

**Colour Test for Cineol.** E. J. Schorn. (*Pharm. J.*, 1925, **114**, 232–233.)—

One c.c. of a 15 per cent. solution of ammonium molybdate in dilute nitric acid containing 5 per cent. of ammonium sulphate, added to varying amounts of 10 per cent. solutions of cineol in alcohol gave blue colorations, and, on comparing equal volumes in Nessler tubes, the colours were found to be proportional to the amount of cineol present. D. G. H.

**Iron in Tragacanth.** G. Elliott. (*Pharm. J.*, 1925, **114**, 234–235.)—

Nine samples of tragacanth were found to contain from 0.0015 to 0.01 per cent. of iron. When tragacanth is made up with salicylic acid as preservative a reddish-violet colour may therefore develop. D. G. H.

**Detection of Ethyl Phthalate in Ethyl Alcohol.** J. T. Raleigh and

S. U. Marie. (*J. Amer. Chem. Soc.*, 1925, **47**, 589–590.)—The U.S. Government official test for the detection of ethyl phthalate in ethyl alcohol, depending on fusion with sodium hydroxide and treatment with resorcinol to form fluorescein, is found to be unreliable, as it gives a distinct fluorescence in absence of ethyl phthalate. The following test, although not conclusive, gives strongly indicative results:—One hundred c.c. of the alcohol are evaporated to small bulk and then poured into a large volume of water containing a few c.c. of sodium hydroxide solution; a milky cloud of ethyl phthalate will develop if this denaturant is present. The boiling point of the ester (290–297° C.) serves as a confirmatory test.

T. H. P.



**The Value of the D.M. Index for Arsenobenzenes.** A. Valeur and L. Launoy. (*J. Pharm. Chim.*, 1925, 1, 4-22.)—The generally adopted limit of 19 to 21 per cent. for arsenic in arsenobenzenes is probably correct, but the ratio of arsenic to nitrogen is not of much value as a criterion of the product. The D.M. index itself (*ANALYST*, 1924, 49, 43) is an empirical figure, which lacks sharp chemical definition, and even when the exact conditions laid down are followed, variable results are obtained. The only satisfactory way of examining arsenobenzenes is by physiological methods.

D. G. H.

**Rapid Microchemical Identification of Novocaine.** G. Denigès. (*J. Pharm. Chim.*, 1925, 1, 32.)—A few particles of the solid are dissolved in a drop of water (in the case of the free base by addition of a trace of acetic acid), and an equal volume of 5 per cent. sodium perchlorate solution is introduced into the centre of the drop by means of a narrow glass tube. Novocaine perchlorate shows characteristic prismatic needles when viewed under the microscope, and the identification is confirmed by the precipitation of silver chloride by means of silver nitrate solution.

D. G. H.

**Constitution and Chemical Properties of the Alkaloids of the Calabar Bean.** E. Cattelain. (*J. Pharm. Chim.*, 1925, 1, 59-69.)—Max and Polonovski, working on eserine (phytostigmine) discovered its oxide, geneserine, and have established the fact that these substances are the methyl urethanes of the nitrogen bases eseroline and geneseroline. They contain one benzene and two heterocyclic nuclei. Geneserine is formed by oxidation of eserine and is readily reduced again, the oxygen being directly linked to the pentavalent nitrogen atom, as in oxamines. In the plant it is formed from eserine by enzymic oxidation. Eseroline and geneseroline form two open chain nitrogen bases as degradation products, *viz.* eserolene (of which the ethoxyl compound is the only known derivative) and  $\psi$ -geneserolene.

D. G. H.

**Therapeutic Value of Extract of Ergot of Rye.** A. Goris and A. Liot. (*Bull. Sci. Pharmacol.*, 1924, 31, 379-390; *J. Pharm. Chim.*, 1925, 1, 123-125.)—Aqueous extraction of powdered ergot of rye only withdraws a small proportion of the specific alkaloids, which is not appreciably increased by the addition of tartaric acid, the extract being naturally acid owing to the presence of hydrogen potassium phosphate. Further evaporation of the aqueous extract causes a certain amount of decomposition of the ergotinine, so that a powder containing 0.167 per cent. of alkaloid gave an extract containing only 0.242 per cent. of alkaloid, whereas it should theoretically have contained 1.2 per cent. The therapeutic action is due not only to ergotinine and other alkaloid bases, but also to amino bases formed during the preparation of the extract.

D. G. H.

**Detection of *Atractylis gummifera* in Liquorice Extract.** P. Bertolo. (*Giorn. Chim. Ind. Appl.*, 1925, 7, 12-14.)—The author maintains the superiority of his method over that proposed by Giuffrè (*ANALYST*, 1923, 48, 30; 1924, 49, 534), which gives uncertain indications.

T. H. P.

## Biochemical, Bacteriological, etc.

**The Nitrogenous Groups of Plant Nucleic Acid.** W. Jones and M. E. Perkins. (*J. Biol. Chem.*, 1925, **62**, 557-564.)—When yeast nucleic acid is treated with dilute sodium hydroxide at room temperature it is decomposed into its nucleotides without the formation of any free phosphoric acid or free purine bases, and deamination does not occur. Experiments carried out by the authors are described, and tables of the results are given. Among the products three of the hitherto accredited nucleotides of yeast nucleic acid (guanine nucleotide, adenine nucleotide and cytosine nucleotide) can easily be isolated in quantity, but the fourth nucleotide (uracil nucleotide) cannot be found. This is especially remarkable because, of the four nucleotides, uracil nucleotide is the one least likely to be lost in analysis, on account of the great insolubility of its brucine salt in 35 per cent. alcohol. A large and unexpected amount of cytosine nucleotide is produced. The conclusion seems obvious: that the oxy-pyrimidine derivatives (uracil, uracil nucleoside and uracil nucleotide), which have hitherto been obtained from yeast nucleic acid, are not referable to an oxy-pyrimidine group in nucleic acid, but are secondary products formed during hydrolysis by deamination of the corresponding cytosine derivatives or their precursors.

P. H. P.

**Studies on Enzyme Action. XXX. Comparative Study of Characteristic Lipase Actions of Tissues of Different Animals and of some Human Tissues.** K. G. Falk, H. M. Noyes and K. Sugiura. (*J. Biol. Chem.*, 1925, **62**, 697-709.)—The average "pictures" of the lipase actions on ten esters of nine tissues of the rat, rabbit, ox, man, and dog (one tissue) are compared in a series of figures. The study of the type of action or "picture" of the ester-hydrolysing actions of a given tissue of an animal together with the absolute actions, both under standard conditions, may be taken to be characteristic in most cases. Definite similarities and differences are pointed out. It is impossible to state definite rules as to the magnitudes of the actions for the same tissue in different animals because of the differences in relative actions on the various esters. As a rule, the rat tissues are the most active, followed by rabbit, beef and human tissues in the order named. This applies to the special experimental conditions used and only in the most general terms. As for the absolute actions of the various tissues of the different animals, the only general statements which may be given point to the facts that the brain and muscle tissues show the smallest actions. A discussion of the results is given.

P. H. P.

**Fat-Soluble Vitamins. XXI. Observations Bearing on the Alleged Induction of Growth-Promoting Properties in Air by Irradiation with Ultra-Violet Light.** E. M. Nelson and H. Steenbock. (*J. Biol. Chem.*, 1925, **62**, 575-593.)—The work carried out by the authors is described fully, and charts and tables show the results. Confirmatory evidence is offered that irradiated rats put in the same cage with non-irradiated rats are able to induce growth in

the latter, even when kept on screens to minimise consumption of excreta. Evidence is also presented that mere irradiation of the false screen bottoms of rat cages is sufficient to induce normal growth in rats when they are kept on a ration deficient in the antirachitic vitamin. No evidence was obtained that the above-mentioned reactions were brought about by secondary radiations acting externally upon the animals, nor that irradiation with ultra-violet light will confer growth-promoting or antirachitic properties on air. It is suggested that the antirachitic growth-promoting reaction was induced in the animals by the ingestion of photochemically activated constituents of the excreta.

P. H. P.

### Germicidal Action of different H-ion Concentrations on Bacteria.

**S. Sierakowski and F. Milejowska.** (*Compt. Rend., Soc. Biol.*, 1924, **91**, 714-715; *Chem. Abst.*, 1925, **19**, 90-91.)—The action of H-ions on micro-organisms is very rapid, and is increased by raising the temperature. By changing the temperature from 20° C. (?) to 45° C. the  $P_H$  at which typhoid bacilli are killed shifts from 4.2 to 5.1. Some of the organisms tested are given in the following list:

Species.	$P_H$ range of tolerance.	Species.	$P_H$ range of tolerance.
<i>B. coli</i>	3.8-10.02	<i>B. rhinosclerome</i>	4.4-10.02
<i>B. typhoid</i>	4.2-10.02	<i>B. ozene</i>	4.8-10.95
<i>B. paratyphoid A</i>	4.0-10.45	<i>B. Friedlander</i>	3.8-10.02
<i>B. paratyphoid B</i>	3.8-10.02	<i>St. aureus</i>	3.9-12.2
<i>B. paratyphoid C</i>	4.1-10.95	<i>St. citreus</i>	4.1-11.92
<i>B. shiga</i>	4.2- 9.63	<i>B. anthrax</i>	1.7-13.0
<i>B. Flexner</i>	4.6- 9.63	<i>B. diphtheria</i>	4.9-10.0
<i>B. cholera</i>	5.3-10.45	<i>B. pseudodiphtheria</i>	5.3-11.31

**Measurement of Chemical Action in Micro-organisms, especially in Yeast.** **T. Bokorny.** (*Allg. Brauer. u. Hopfenzeit.*, 1924, 7-9; *Chem. Abst.*, 1924, **18**, 3409.)—Experiments have shown that a definite amount of poison is required for a definite amount of living cell substance, and that the poison and living substance combine chemically in proportionate amounts. No cases were observed where a combination of poison and cells did not occur. The combination with the poison varies greatly with the amount, and especially with the active concentration of the poison, according to the kind of bacteria or yeast. It is recommended that in practice both the lethal dose and the activity of different dilutions of a disinfectant should be indicated. For example, in the case of formalin: lethal dose for 10 grms. of pressed yeast containing 25 per cent. of dry substance =  $x$  grms.; active dilution from 7 per cent. upwards; the velocity of the reaction varies with the degree of the dilution, and the poisonous action increases with increase of temperature.

**Determination of Lecithin in Blood.** **A. Grigaut.** (*J. Pharm. Chim.*, 1925, **1**, 97-104.)—The determination is made by means of a colour reaction based on the fact that phosphomolybdic acid in the presence of suitable reducing agents gives a blue colour, and that, under certain conditions, the excess of

molybdc acid is without effect on the coloration. One c.c. of blood serum is poured, drop by drop, with shaking, into 40–50 c.c. of a mixture of 3 parts of 95 per cent. alcohol and 1 part of ether, and, after 10 minutes, filtered through an ashless paper which is then washed with further portions of ether. The united extracts are evaporated just to dryness, and the residue taken up while still warm with dry ether, filtered or centrifuged, the paper washed, and the ethereal solution transferred to a Kjeldahl flask and evaporated to dryness. A few c.c. of distilled water, 1 c.c. of concentrated nitric acid, and 1 c.c. of sulphuric acid (sp. gr. 1·843) and a glass bead are added in succession, and the mixture boiled. As soon as the water has disappeared and when fumes appear, the flame is lowered and heating continued until the solution is colourless. After cooling, 30 c.c. of distilled water are added and boiled down to 10 c.c. (to ensure pyro- and meta-phosphates being transformed to orthophosphates), and the contents are then transferred to a 50 c.c. graduated flask, made up to about 40 c.c. and neutralised with 40 per cent. sodium hydroxide solution. Five c.c. of the standard solution of phosphate (containing 0·044369 gm. per litre of  $\text{NH}_4\text{H}_2\text{PO}_4$ ; equivalent to 1·5 mgrm. of lecithin in 5 c.c.) and the same volume of sodium hydroxide solution as was used above, are put into another 50 c.c. flask, and neutralised with dilute sulphuric acid. The cooled solutions are each made up to 50 c.c., and 2 c.c. of the sulpho-molybdc reagent (containing equal parts of 10 per cent. ammonium molybdate and sulphuric acid of sp. gr. 1·843) 0·5 c.c. of the stannous reagent (0·1 gm. of tin foil dissolved in 2 c.c. of concentrated hydrochloric acid and 10 c.c. of distilled water) are added. After 2 minutes the colours are compared in a Duboscq colorimeter. Then the percentage of lecithin in the serum is  $1\cdot5 \times E/S$  grms., where E is the depth of the type solution and S the depth at which the solution under examination shows the same tint.

D. G. H.

**Method for Determining Methæmoglobin in the Presence of its Cleavage Products.** J. B. Conant and L. F. Fieser. (*J. Biol. Chem.*, 1925, 62, 623–631.)—As a spectrophotometer is not always available, a method has been developed for determining methæmoglobin in the presence of its cleavage products or other coloured material. It consists in measuring the increase in oxygen capacity, resulting from the action of a powerful reducing agent which quantitatively converts the methæmoglobin to haemoglobin. Sodium anthrahydroquinone- $\beta$ -sulphonate is a satisfactory reducing agent for this purpose, although the oxygen capacity after reduction must be determined rapidly, and the equilibration with pure oxygen must be of very short duration. Disodium anthrahydroquinone-2,6-disulphonate is a somewhat less satisfactory reagent whilst sodium hyposulphite cannot be used at all because its oxidation products catalyse so greatly the re-formation of methæmoglobin. In the calculation one really measures the amount of material which by itself has no oxygen capacity, but which, after treatment with a reducing agent, combines with oxygen reversibly. As far as is known, the only substance which has this very peculiar property is methæmoglobin.

P. H. P.

**Effect of Sodium Benzoate Ingestion upon the Composition of the Blood and Urine, with especial Reference to the Possible Synthesis of Glycine in the Body.** W. W. Swanson. (*J. Biol. Chem.*, 1925, 62, 565-573.)—

Experiments, described in detail, were made to obtain values for the non-protein nitrogen constituents in the blood and urine found by simultaneous analyses after ingestion of sodium benzoate, and to investigate what bearing, if any, these values may have on the synthetic ability of the human body to produce glycine for conjugation with the benzoic acid. Analyses show:—(1) No increase in the urea nitrogen content of the whole blood and plasma, but a decrease in the urea nitrogen content of the urine; (2) an increase of the uric acid content of the whole blood and plasma, and a marked decrease in the uric acid content of the urine; (3) the glycine portion of the blood amino acids and of those which are normally excreted while fasting appears to be only a small percentage, if any, of the total; and (4) the experimental findings suggest a probable synthesis of glycine from the constituents which normally are converted into urea, but it appears improbable that uric acid supplies any glycine. The results are discussed.

P. H. P.

**Detection of Amino-nitrophenols in Urine.** L. Desvergnés. (*J. Pharm. Chim.*, 1925, 1, 56-59.)—

The Derrien azo reaction cannot be applied directly to the urines of persons absorbing iodine or iodised peptones, owing to the masking of the colour developed, and it is necessary in such cases to add 2 drops of sulphuric acid to 5 c.c. of urine, extract three times with chloroform, filter and then proceed with the test. To 10 c.c. of the filtrate are added 1.5 c.c. of a 0.5 per cent. sodium nitrite solution, and, after 10 minutes' contact in very cold water, the mixture is poured into 1 c.c. of a freshly prepared solution of 0.5 per cent. ammoniacal  $\beta$ -naphthol. After a few minutes 10 c.c. of ether are added, and the mixture gently shaken, after which a pale pink to red-violet colour indicates the presence of amino nitrophenols in the urine.

D. G. H.

## Toxicological and Forensic.

**The Arsenic Content of Baking Powder.** S. Goy and A. Köhler.

(*Chem. Zeit.*, 1925, 49, 189.)—In consequence of a case of arsenical poisoning in Breslau, traced to the use of potassium carbonate as baking powder, a series of 68 samples from that town and province was examined, and 12 were found to contain arsenic ranging in amount from 0.09 per cent. to 0.38 per cent. as  $As_2O_5$  (no arsenic was present in the arsenious condition). This amount would be poisonous if the potassium carbonate were used as a baking powder. The arsenic originates in the arsenical dips used for sheep, from the wool of which the potassium carbonate is prepared. It is also pointed out that fellmonger's wool coming from skins which have been unhaired (de-wooled) with lime and arsenic paints may be another source of arsenic contamination. Of 133 baking powders not made with potassium carbonate, none was found to contain arsenic.

R. F. I.

**Toxic Action of Commercial Ether.** E. Remy and F. Neuhart. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, **48**, 445-449.)—During investigation of a cocoa alleged to have caused sickness, physiological experiments were made by injection of some of the ether-extracted fat and of aqueous extracts into mice. The ether extract in each case caused poisoning, but not so the aqueous extracts. It was found that the ether left a residue on evaporation amounting to 0.03 per cent., which contained dioxyethyl-peroxide and vinyl alcohol, both of which were proved to be highly toxic. The vinyl alcohol may be detected by shaking 50 c.c. of the ether with 9 c.c. of potassium bicarbonate solution and 20 c.c. of mercuric chloride solution, when a white amorphous precipitate of  $\text{Hg}_3\text{Cl}_2\text{O}_2\text{C}_2\text{H}_3$  is given in the presence of this alcohol. Dioxyethyl-peroxide is detected by means of potassium iodide. It is evidently essential to employ only the purest ether for extractions which are to be used for physiological experiments. H. E. C.

## Organic Analysis.

**Rapid Method for Determining Carbon in Organic Compounds.** H. D. Wilde (jun.) and H. L. Lochte. (*J. Amer. Chem. Soc.*, 1924, **47**, 440-446.)—The compound is burnt in presence of compressed oxygen and of standard barium hydroxide solution (0.5 *N*) in the calorimetric bomb, the carbon dioxide thus formed being absorbed by the alkali when the bomb is subsequently shaken. The solution is then titrated with 0.5 *N* hydrochloric acid in presence first of phenolphthalein and then of methyl orange, the amount of acid required between the two end-points being equivalent to the carbon dioxide formed. If the operations are carried out rapidly in a well ventilated laboratory, the carbon dioxide of the air may be neglected. Solid substances should be compressed into pellet form before weighing and, if difficult to burn completely, should be placed in an ordinary gelatin capsule, this being previously weighed. Such capsules, which are hygroscopic and should be stored in a desiccator, are of uniform carbon content, so that the necessary correction is readily determined. Liquids may be weighed in the capsules except when these are rapidly attacked; in such case one of the regular methods of burning liquids for calorimetric purposes must be used. If the compound contains sulphur, this may be determined gravimetrically in the titrated solution. Nitrogen from nitrogenated compounds does not interfere with the carbon determination and seems to escape almost entirely as free nitrogen.

Compounds containing halogens, however, require special treatment, oxyhalogen compounds, present in the alkali after the combustion, being destroyed by a reducing agent, such as hydrazine hydrate, the solution being then acidified and boiled, and the carbon dioxide thus liberated reabsorbed by barium hydroxide before titration.

The above procedure gives excellent results with compounds difficult or impossible to burn completely by the ordinary combustion method. T. H. P.

**Application of Sodium Hyposulphite (Hydrosulphite) in Organic Analysis.** E. Clark. (*Chem. News*, 1925, 130, 132.)—In establishing the benzenoid nature of a compound by the usual method the very bulky precipitate of zinc hydroxide may altogether mask the formation of the red hydroxy-azo compound. Instead of using zinc and hydrochloric acid as the reducing agent for the nitro-body, the author has found great advantage in using sodium hyposulphite in alkaline solution. The supposed benzenoid compound is nitrated in a test-tube as usual, and the product cooled and made alkaline with sodium hydroxide. To the alkaline solution is added a small amount of solid sodium hyposulphite, with shaking. The mixture is then heated to boiling, acidified with excess of hydrochloric acid, and boiled till all smell of sulphur dioxide has disappeared. The solution is then cooled, treated with a few drops of sodium nitrite solution and added to alkaline naphtholate solution, when a brilliant red colour results if the original substance was of aromatic character. Nitro-compound  $\rightarrow$  sulphonic derivative of the amino compound  $\rightarrow$  amine hydrochloride  $\rightarrow$  diazonium compound  $\rightarrow$  red hydroxyazo compound. R. F. I.

**Occurrence of Free Pentoses in Plants. Effect of Extraction of the Sugars with Ammoniacal Alcohol.** D. T. Englis and C. Hale. (*J. Amer. Chem. Soc.*, 1924, 47, 446-449.)—After subjection to prolonged heating with ammoniacal alcohol in a reflux apparatus and to considerable concentration under reduced pressure, an alcoholic solution containing sucrose and invert sugar appears to contain appreciable amounts of pentoses when tested by either the Krobber-Tollens or the fermentation method. In absence of ammonia the above treatment gives no apparent pentose according to the fermentation method, but a small quantity by the other method of testing. The amounts of pentose found are not sufficient to account for the total quantities reported in plant extracts, but it is evident that any method of extracting sugars which involves the use of ammonia and, possibly, other weak alkali, should be avoided or used with caution.

T. H. P.

## Inorganic Analysis.

**Volumetric Determination of  $Pb_3O_4$  in Red Lead.** E. F. Figg. (*J. Soc. Chem. Ind.*, 1925, 44, 68T.)—To 1 gm. of red lead in a glass mortar are added 40 c.c. of a saturated solution of sodium acetate in 5 per cent. acetic acid, and a known excess (40-50 c.c.) of 0.1 N sodium thiosulphate solution. Rubbing is carried on until all undecomposed red lead has disappeared, and the addition of a few c.c. of 5 per cent. potassium iodide solution hastens the reaction. Starch solution is added, and the excess of thiosulphate solution is then determined by titration with 0.1 N iodine solution. The excess of sodium acetate prevents precipitation of lead iodide, and the end-point is sharp. D. G. H.

**The Alloxantin Reaction for Ferric Iron.** G. Denigès. (*Compt. Rend.*, 1925, 180, 519-520.)—Alloxantin forms an exceedingly delicate reagent for ferric iron when present as a complex ion, such as citric and tartaric compounds, which

do not react with the ordinary reagents. The reagent should be freshly prepared by dissolving 0.1 grm. of alloxantin in 10 c.c. of *N* sodium hydroxide solution. If the solution has a pink colour, it should be boiled until the colour just disappears, then cooled. The reagent is now added to the solution containing the iron, and a blue colour is obtained in the presence of 1 mgrm. of iron per litre. By using a larger volume of solution the reaction can be made much more delicate. The presence of alkalis or organic acids does not interfere. H. E. C.

**Separation of Zinc and Nickel by Hydrogen Sulphide.** A. Kling and A. Lassieur. (*Compt. Rend.*, 1925, 180, 517-519.)—By careful attention to the acidity it is possible to precipitate zinc sulphide alone in the presence of nickel. The solution must be acidified with acetic acid and controlled by ammonium salts. Hydrogen sulphide must be boiled off before the  $P_H$  is determined, as it interferes both with a hydrogen electrode and with indicators. It is found that nickel is completely precipitated only when the  $P_H$  lies between 2.8 and complete neutrality. Zinc is precipitated in 45 minutes when the  $P_H$  is at 2.4. The presence of salts disturbs these values. H. E. C.

**Electrolytic Determination of Zinc in Alloys.** J. W. Springer. (*Zeitsch. anal. Chem.*, 1925, 65, 315-317.)—One grm. of brass or bronze is dissolved in strong nitric acid, the solution diluted slightly and treated with enough ammonia to redissolve the precipitate. The solution is filtered, if necessary, and the filtrate neutralised with sulphuric acid (1:1) and treated with 10 c.c. excess. The copper is deposited from the boiling solution by a current of 4 amp.; the electrolyte is neutralised with sodium hydroxide, of which an excess of 10 grms. is added. The solution is electrolysed at a temperature near the boiling-point with a current of 4 amps. for 15 to 20 minutes, the platinum wire anode rotating at 800-1000 R.P.M. The amalgamated brass gauze cathode is washed without interruption of the current, rinsed with alcohol, and dried at 70° to 80° C. The results are stated to be good (*cf.* ANALYST, 1924, 49, 403). W. R. S.

**Elimination of Phosphoric Acid in Qualitative Analysis by Bismuth Subnitrate.** A. Keschan. (*Zeitsch. anal. Chem.*, 1925, 65, 346-351.)—The filtrate from the hydrogen sulphide precipitate is evaporated almost to dryness and again evaporated to small bulk with nitric acid to eliminate most of the hydrochloric acid. If iron is present, the solution is diluted with 10 to 15 volumes of water, saturated with hydrogen sulphide, treated with excess of solid bismuth subnitrate, boiled and diluted with an equal volume of hydrogen sulphide water. It is left to cool somewhat and filtered warm. Iron in the ferric condition would prevent the complete precipitation of the phosphoric acid through formation of complex anions; the hydrogen sulphide is added as reducing agent. A certain amount of bismuth sulphide is formed, but this is mostly converted into nitrate in the boiling liquid. The precipitate, which is removed by filtration, should always be discoloured by sulphide, which shows that the iron remains reduced; if necessary, more hydrogen sulphide water must be added. The iron may also be reduced by hydrazine



hydrochloride. If iron is absent, the required excess of bismuth subnitrate is at once added to the concentrated nitrate solution after evaporation; the mass is then diluted gradually with 20 to 30 volumes of water and boiled until a small filtered portion gives no reaction with molybdate mixture. If the reaction persists after 15 to 30 minutes, more subnitrate must be added.

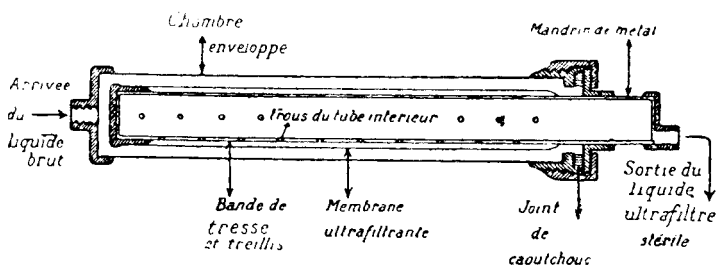
W. R. S.

## Physical Methods, Apparatus, etc.

**Spectrophotometric Determination of  $P_H$ .** F. Vlès. (*Compt. Rend.*, 1925, 180, 584-586.)—Spectrophotometric methods of determining  $P_H$  (*cf.* Holmes, *ANALYST*, 1924, 49, 253) suffer from the disadvantage that the absorption of the indicator,  $\log(I/I_0)$ , is a function of two independent variables, namely  $P_H$  and the concentration of the indicator, so that an awkward readjustment becomes necessary on every occasion when there is divergence from the standard experimental conditions. For indicators composed of two tautomeric spectral components and for values of  $P_H$  which are not extremely low, it is shown that the concentration of the hydrogen ions may be expressed as a function of the ratio of the absorptions for two different wave lengths, and independently of the concentration of the indicator, preliminary empirical standardisation being unnecessary. The relation found is applicable in practice to some indicators, but with others, such as crystal violet, anomalous behaviour is observed owing to the transformation, between the values 3 and 1 of  $P_H$ , of the violet form ( $\lambda 592$ ) into the green form ( $\lambda 632$ ), which then undergoes progressive destruction to give a yellowish form.

T. H. P.

**A Collodion Membrane Ultra-filter. Physico-Chemical Analysis of Solutions.** E. Fouard. (*Ann. Chim. anal.*, 1925, 7, 33-34.)—The apparatus



shown in the figure has been devised so that a collodion membrane can be used for ultrafiltration in such a way that it cannot lose its shape and can withstand pressures (up to 40 atmos.) without any alteration in its properties. The apparatus consists of a rigid body, an enamelled metal tubular mandrel, protected against different reagents, and with small holes evenly distributed over its surface; this is bound with an artificial silk braid and over it is fixed a lattice-work of

strong thread with a large mesh of 1 or 2 mm. The whole is closed at one end and open at the other. By a special technique, a covering of collodion, which does not penetrate the envelope of braid, but completely immerses the meshes of the network of thread, is placed on the system, thus, by the coagulating effect of the water, forming a membrane (which is no longer fragile but strong owing to the mesh) all over the surface. The whole apparatus is placed in a metal case, so that it can be fixed in a pressure chamber. Ultra-filtration takes place from the exterior to the interior of the mandrel. This apparatus can be used regularly for a year for sterilising water without needing attention.

P. H. P.

**New Method for Examining the Interior of Pearls.** B. Szilard. (*Compt. Rend.*, 1925, 180, 433-436.)—This method, which is applicable to pearls, bones, fibres, wood, etc., consists in examining the object when completely immersed in a liquid of suitable refractive index and strongly illuminated from below. The liquid serves to prevent the reflection of the light from the surface, so that the rays actually penetrate the object. Over an electric lamp is placed a flat cell containing water (to keep the condenser cool), then an optical condenser, and then the pearl immersed in cedar-wood oil; over this is a diaphragm and finally the low-power lens of a microscope. In the case of pearls it is distinctive that in cultivated pearls there are visible, in the interior, concentric striations corresponding to the layers formed by the deposition of the mother-of-pearl. In genuine natural pearls these striations are absent. Diagrams and photographs are given.

H. E. C.

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#### ERRATUM.

**Hydrogen Ion Concentration of Natural Waters.** ANALYST 1923, 48, 397, line 3: for " $P_H = 6.3$ " read " $P_H = 8.3$ ."

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### Reviews.

A SYSTEM OF PHYSICAL CHEMISTRY. Vol. III. QUANTUM THEORY (Third Edition). By WILLIAM C. Mc. C. LEWIS. Pp. x. +410 (with 24 figures). London: Longmans, Green & Co. 1924. Price 15s.

The application of the quantum mechanism to the elucidation of the phenomena attending the interconversion of atomic and radiant energies has led us to the conclusion that the structures of atoms change in a discontinuous manner as their energy content increases. Thus it would appear that the individual atoms of a mono-atomic gas differ from one another, not only in respect of their velocities of translation, but also in regard to their internal structures. The extension of this view to molecules introduces a conception into chemistry the influence of

which will undoubtedly be comparable with that of Dalton's atomic theory, over a hundred years ago.

Physical chemists have been aware, almost from the beginnings of the quantum theory, of its importance for the study of the kinetics of chemical change, and Professor Lewis was one of the first to advocate its application to chemistry. On the other hand, the majority of chemists do not appear to have grasped its significance for the interpretation of the constitution of chemical compounds. Deductions as to constitution based on chemical behaviour are very frequently at variance with those arrived at from a study of physical properties, for chemical behaviour is determined by the constitution of an extremely small fraction of the total number of molecules present, namely, those in a specially active state, whereas all of the molecules contribute their quota in any physical measurement. The application of quantum considerations should throw light, not only on the active, but also on the other molecular states present in a chemical system.

Professor Lewis's book has already played a great part in the development of the more recent views of chemical behaviour, and the new enlarged edition is very welcome. The present edition is twice the size of that issued in 1919, and this increase in size is an indication of the rapid rate of development of the subject covered by the volume. It has been entirely re-written, except for the first few chapters, which have been thoroughly revised. The increase in size is partly due, however, to eight appendices at the end of the book. The paper on which it is printed is a great improvement on that of the 1919 edition, and the publishers are to be congratulated on the low price at which the work is issued.

The scope of the book is very wide and includes accounts of nearly all of the recent physical investigations which have, or are likely to have, any bearing on chemistry. The selection of the material from the original papers and its arrangement in the form of a coherent argument has been a difficult task, for it is not always possible to correlate work done in isolated fields. In the first two chapters, which deal with the interchange of energy between resonators and radiation, it is shown how the failure of the equipartition principle led to the introduction by Planck of the quantum theory. This is then applied to the energy contents of solids and gases, the equations of Einstein, Nernst-Lindemann, and Debye being given. A very interesting summary on mono- and di-atomic gases and of the degradation of gases from the point of view of the quantum theory is included. In the chapter on atomic and molecular structure, the Bjerrum and Kratzer theories of infra-red band spectra and the various atomic models, due to Bohr, Langmuir, Whittaker, etc., are points of special interest. The work of Henri and others on the molecular structure of organic compounds, which should have appeared in this place, has been ignored, and the space afforded to the orbits of the electrons in the chemical bond (three pages) appears to be unduly small, considering the importance of the question.

The application of the quantum theory to volatilisation, sublimation, and fusion, the thermionic and photo-electric effects, and ionisation and resonance

potentials receive their due attention. Chemical reactivity, both thermal and photochemical, is treated very fully, largely from the point of view of the radiation hypothesis, in regard to which the author has summarised the evidence both for and against. The author's development of this section is open to criticism, in that he takes an extreme view of chemical reactivity; he has, on the strength of the difficulties inherent in explanations of the mechanism of the hypothetical monomolecular reaction, eliminated kinetic energy of translation from his considerations. Even if chemical change is limited to those collisions occurring between active molecules, it is not certain that the speeds on collision of all of these are sufficient for the penetration of the first line of defence, the outer envelope of the molecule. A minimum kinetic energy would appear to be necessary which, it is true, may be so low in a number of reactions that all collisions between active molecules are fruitful, and the  $A$  in the Arrhenius equation equals  $h\nu$ , where  $\nu$  is the frequency of the radiation activating the molecule. In the majority of the reactions studied, however, this is certainly not true.

The energetics of crystal structure, including the affinity of atoms for electrons, and atoms for atoms, is dealt with in Chapter VIII., and a short account of molecular and atomic forces is given. The bearing of the quantum theory on the Nernst heat theorem, chemical constants, and mass action equilibria forms the last chapter.

Appendices on special points not referred to in detail in the text are given at the end of the volume, including Maxwell's distribution law, the quantum theory, and the correspondence principle by James Rice, on the Sommerfeld-Bohr theory by A. McKeown, and on Einstein's law of the photochemical equivalent by R. O. Griffith.

The volume contains in a small compass an account of the modern developments based on the quantum theory, and as a book of reference will prove of great service. It is essentially a monograph, not a text book in the true sense of the word. It is to be doubted if the time is yet ripe for a text book on this subject, especially as the body of knowledge within its purview is undergoing such rapid changes.

W. E. GARNER.

L'ORIGINE TOURBILLONNAIRE DE L'ATOME ET SES CONSÉQUENCES. PAR JEAN VARIN D'AINVELLE. Paris: Gauthier-Villars et Cie. Pp. 214. Price 10 fr.

The vortical origin of the atom, if indeed its origin be vortical, has attracted but little attention in the present century. Physicists and chemists have devoted their energies rather to the study of the actual and ascertainable properties of atoms and their constituents than to speculations as to their origin. The author of this book has revived a theory which may recall to some readers the Helmholtz Memorial Lecture given by Fitzgerald in 1896. He said: "To the Chemical Society the question of most importance is how Helmholtz's work bears on chemical theories. Unfortunately, there is very little really known about this in respect of vortex motion. Lord Kelvin has made the brilliant suggestion that atoms are

vortex rings, and upon this all subsequent guesses have been founded; for our knowledge in this direction is very little better than guesses. Helmholtz had shown that vortices in a perfect liquid could neither create nor destroy one another. Once created, a vortex ring is permanent like an atom of matter." On this "correspondence principle" the vortical theory of the nature of atoms is based.

Clearly atoms must have had some origin. The ether is a convenient conception furnishing a means of evading the difficulties of action at a distance and, as the late Lord Salisbury said to the British Association, providing a nominative to the verb "to oscillate." Vortices in such a fluid would have all the permanence attributed to atoms and would differ from the circumambient ether only by reason of their motion and not qualitatively. A merely dynamical origin of matter is thus made possible, and we have a homogeneous etherous universe.

The vortical theory is not without its difficulties. Fitzgerald pointed out that it is difficult to fit in the constancy of the relation of gravitation and inertia at varying temperatures with the vortex theory. This and other difficulties led Fitzgerald to "prefer in our ignorance the horn of the dilemma, that holds that atoms are not simple thin vortex rings in an otherwise unmoving liquid."

M. Varin D'Ainvelle says: "Je vais essayer dans cet ouvrage de déduire les lois de la Physique de l'hypothèse suivante: les atomes sont des tubes de tourbillon nés et se mouvant dans l'éther, fluide auquel nous n'attribuons aucune propriété spéciale comme le serait une rigidité anormale, mais qui ressemble aux fluides réels ordinaires, étant comme eux visqueux, compressible et sujet à des changements de température. Il est seulement plus subtil que n'importe quel fluide connu, en entendant simplement par là que ses molécules sont fort petites et très peu denses. Les qualités énumérées plus haut ont un ordre de grandeur en rapport avec cette subtilité. On peut dire que l'éther ainsi conçu répond à la conception intuitive que nous nous en faisons."

The Bohr or Langmuir atom is a gross and all too simple structure compared with our author's "tourbillon E" or hydrogen atom. Brought into being by the encounter of two currents of ether, the atoms of the universe started as thin vortex rings which on rupture became hollow cylinders, and will finally, like those larger vortices, the heavenly bodies, become solid spheroids. The evolution is naturally slow, and our atoms are at present hollow cylinders with which are associated a Newtonian attraction originating from the contraction vector giving rise to *mass*, *magnetism* due to the vector of translation, and *electricity* due to the vortex vector. "Nous pouvons donc donner cette définition de la matière: c'est la portion de volume de l'éther dont chaque molécule est chargée d'une quantité de *mass*, d'une quantité de *magnétisme*, et d'une quantité de l'électricité: ces quantités, toujours les mêmes et indépendantes les unes des autres, sont des constantes de la nature. Les propriétés qui en découlent sont additives. La réunion d'un certain nombre de telles molécules constitue un atome de matière ou tourbillon E. Ce nombre est constant, mais non rigoureusement. Il subit des fluctuations autour d'une valeur moyenne."

Having endowed his atoms with their necessary properties, the author finds no difficulty in accounting for those of matter. He strays occasionally into cosmogony and metaphysics. It is all very clever, but it is difficult to feel that it has any relation to that which is. The atom and the electron may be said to be real. The quantum has been a fertile and necessary conception. Hard particles may be, as Fitzgerald said, "an abomination." If one could only think of the harmless necessary\* ether as a continuum all would be well—except perhaps many theories. The necessity of giving it convenient properties has led to a jelly, a foam, and a lattice structure being ascribed to ether. The author considers it as a series of fluids made up of molecules, each fluid being finer grained than that which is buoyed in it. This seems to give an unending series of hard particles. One is reminded of William of Occum's Razor, "Entia non sunt multiplicanda praeter necessitatem."

For one modern concept M. Varin D'Ainvelle has no use, the positive nucleus. His "tourbillons T" or electrons serve all his purpose. The positive nucleus is none other than the atom deprived of its electron. For us negative electricity has the electron for its atom, and positive electricity does not exist. The positive ion is the atom deprived of an electron. This "one fluid theory," as it were, is made feasible by his very complicated atom.

As to Einstein's theory of relativity the author is neutral. So far he needs it not, but he has not found it necessary to repudiate it. He can take it when he feels disposed.

It is impossible to do justice to a book of this kind within the limits of an ordinary review. Those who are attracted will, perhaps, read it and devise tests for the theory propounded. One wonders are such books written from a feeling of the need of an explanation of phenomena or as rhapsodies in mathematical metaphysics. It may all be true, but, alas, how very complicated. One feels the profundity of the words which Oliver Heaviside, who died within the last few weeks, wrote years ago: "Even if we resolve all matter into one kind, that kind will need explaining. And so on, for ever and ever, deeper down into the pit at whose bottom truth lies, without ever reaching it."

J. H. COSTE.

THE CONSTITUENTS OF COAL TAR. By P. E. SPIELMAN, Ph.D., F.I.C. Pp. xii. + 219. London: Longmans, Green & Co. 1924. Price 12s. 6d.

This volume is the latest in the interesting series of monographs on industrial chemistry edited by the late Sir Edward Thorpe.

The author's object of placing before those chemists interested in the utilisation of coal tar products, a volume containing a summary of the researches of the very large number of workers in this field is a very laudable one. Hitherto short chapters in comprehensive works, such as that of Lunge, have been the only source of information other than the laborious study of current literature. Recently

\* For arguments against the necessity of the ether see Dr. Jeans' Kelvin Lecture (*Nature*, March 7, 1925).

a great deal of work has been carried out on tars of all kinds, particularly in Germany, and this volume, while it does not claim to be encyclopaedic, will serve as a practical guide and as a useful summary of the information available to 1924.

The volume is divided into five parts, the first of which is a general summary of the compounds which occur in tars of different kinds. The other four parts deal with these in their various classes of hydrocarbons, oxygen compounds, etc. The important compounds in each class are treated in detail, their occurrence commented upon, and their physical and chemical properties described at length.

In Part I. the author points out the relation between low and high temperature tars, but, unfortunately, makes no reference to the effect of the type of coal on the composition of the tar. This omission is continued throughout the book, and the reader is continually at fault regarding the nature of the coal used. In some cases, also, tars are described which are by no means representative. For example, some of the data in Table 1 are obviously incorrect (*e.g.* low temperature tar prepared by modern processes has a density of 1.05 not 1.13, and contains much less than 61.4 per cent. of pitch). Considerable amplification of Part I., with particular reference to the different tars available and their properties, would have made the volume much more valuable. In Parts II. to V. this could have been followed up by mentioning in the generalised statements the class of coal and the method of tar preparation. The information regarding the different chemical substances described is very well set out and extremely comprehensive but, again, the space devoted to their occurrence is very limited.

The bibliography at the end of the book is good, and its extent (525 pages) is an indication of the trouble which the author has taken to make available to his readers the origin of the many papers on this subject. In some cases where different authors have the same name it is a pity that they are not referred to separately in the index and their initials quoted. Certain errors have crept in as, for example, ref. 12 should read volume 105 instead 104.

The book is well written and printed and should be welcome in the libraries of gas and tar works. When the march of progress calls for a further edition it is to be hoped that the author will make considerable extensions in his treatment of the origin of the tars described and of the variations of compounds in each type.

J. G. KING.

METALLURGY. AN ELEMENTARY TEXT-BOOK. E. L. RHEAD, M.Sc.Tech., F.I.C., A.I.M.E. New Edition. Pp. xii.+403. London: Longmans, Green & Co. 1924. Price 7s. 6d.

The preceding edition of this work having gone through six new impressions, the text-matter has been brought up to date in the present edition by suitable additions and deletions. The book is so well known that a detailed analysis of its contents is unnecessary; in the writer's opinion the author is at his best in the chapters on general metallurgy, iron, steel, and copper, whilst his treatment of the non-ferrous metals (other than copper) and especially some minor metals is not uniformly happy. Mention, however brief, might have been made of such

advances in metallurgical practice as the electrolytic refining of lead, silver, and gold, the combined amalgamation-cyanide process for silver ores practised in Canada, and the modern hydrometallurgy of copper. The metallurgy of aluminium is dismissed in rather less than six lines; this may have been considered adequate thirty years ago, but the present importance of aluminium and the peculiarity of its metallurgy make a more detailed treatment imperative in an up-to-date text-book, even though elementary. The uses of cobalt and its growing importance as an alloy metal are mentioned, but nothing is said about its extraction or occurrence.

A great fault the reviewer has to find with the book is the careless style in which too many passages are written. The following sentence, picked out at random, is a case in point: "In roasting blende containing much iron the solubility of the zinc is diminished by the formation of zinc ferrate" (p. 369). This may be taken to mean that all the zinc is converted into "ferrate," and that it is more difficult to dissolve zinc "ferrate" than the oxide; whereas the author evidently means that part of the zinc is converted into zinc ferrite, which is insoluble in acid, with the result that the recovery, not the solubility, of the zinc is diminished. Under Gold Parting (p. 344) is found the curious term "osm.-iridium," which can hardly be a misprint, as it occurs three times in the same paragraph. Platinum is alleged to occur (p. 380) "with the rare metals, rhodium, osmium, iridium, ruthenium, rubidium" (*sic.*). The terms "quick silber" (p. 287) and "braque" (p. 68) pass for German. Similar minor inaccuracies and misprints are fairly numerous, implying careless proof-reading.

On the whole, it may be said that the revision of the book has been too conservative; obsolete processes have been accorded a little too much space, whilst some modern processes of quite considerable importance have been neglected.

W. R. SCHOELLER.

## Publications Received.

- INDEXED LIST OF BRITISH STANDARD SPECIFICATIONS AND REPORTS (1925).  
British Engineering Standards Association. Price 1s. 2d. post free.
- INTRODUCTION TO ORGANIC RESEARCH. By E. EMMET REED. Constable & Co.  
1925. Price 24s. net.
- YEAR BOOK OF SCIENTIFIC AND LEARNED SOCIETIES (1923-1924). Chas. Griffin  
& Co. Price 15s.
- COLLECTIVE INDEX OF THE JOURNAL OF THE INSTITUTE OF BREWING, 1911-1923.