THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, June 1st, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of Arthur Littlewood, M.A., A.I.C., and John Henry Weber, B.Sc., A.I.C.

Certificates were read for the second time in favour of Charles Carr Marginson, B.Sc., A.I.C., Ph.C., Wilfred Mather, A.M.C.T., F.I C., Alec Duncan Mitchell, D.Sc., F.I.C., and M. Niyogi, M.Sc.

The following were elected Members of the Society:—Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Aluminium in Foods," by L. H. Lampitt, D.Sc., F.I.C., and N. D. Sylvester, M.Sc., A.I.C.; "The Spectrographic Determination of Small Quantities of Aluminium," by P. L. Bilham, B.Sc., A.I.C.; and "The Physiological Effects of Aluminium," by J. H. Burn, M.A., M.D.

Notice was given that a Joint Meeting would be held with the Food Group of the Society of Chemical Industry, on the subject of Changes in Fruit on Storage, on Wednesday, October 5th.

Death

WITH deep regret we record the death, on June 13th, of Mr. Cecil Howard Cribb. An obituary notice will be published in a later issue.

The Determination of Small Amounts of Aluminium in Food

By L. H. LAMPITT, D.Sc., F.I.C., and N. D. SYLVESTER, M.Sc., A.I.C.

WITH A NOTE ON THE SPECTROGRAPHIC METHOD

By P. BILHAM, B.Sc., A.I.C.

(*Read at the Meeting, June* 1, 1932.)

Knowledge of the effect of small quantities of metals or metallic salts on the human organism is assuming an ever-increasing importance, and it follows, therefore, that it is essential to obtain definite information regarding, *inter alia*, the contamination of foodstuffs by containers and cooking utensils. The general question of absorption of metals by animal tissues demands accurate and reliable methods for the determination of small amounts of metals in organic materials.

We claim no more in the present paper than to have standardised a method for the determination of aluminium, and, in view of the difficulties later described with regard to the colour changes, we consider that our application of the Lovibond tintometer to the determination has rendered it sensitive and of a high degree of accuracy.

It is obvious that, for the determination of aluminium in food, two separate problems are involved:—(i) The development of a suitable process for the quantitative determination of the aluminium-content of a solution; (ii) The preparation, in as simple a manner as possible, of a solution containing the aluminium free from any substance which would interfere with the determination.

I. Determination of the Aluminium-Content of a Solution.—Of the various reagents which have been proposed for the detection of small amounts of aluminium, sodium alizarin sulphonate[1] and aurin tricarboxylic acid[2] have received most attention for the quantitative determination. We have investigated both these methods, and have preferred to use aurin tricarboxylic acid, since the colour-change from pale orange to intense red is more easily appreciated and more accurately matched in the Lovibond tintometer than the change from orange-yellow to orange-red, which occurs in the alizarin "S" method.

Aurin tricarboxylic acid was first proposed for the detection of aluminium by Hammett and Sottery,[2] and the details of their original test are as follows:

"To a solution containing the aluminium in 5 c.c. of *N* hydrochloric acid are added 5 c.c. of 3 *N* ammonium acetate and 5 c.c. of a 0·1 per cent. solution of the ammonium salt of aurin tricarboxylic acid. After the formation of the lake the solution is made alkaline with ammonium hydroxide containing ammonium

carbonate. A bright red coloration or precipitate indicates the presence of aluminium."

This reaction has been applied to the quantitative determination of aluminium in organic materials by several workers. Thus, Myers, Mull and Morrison[3] used Nessler tubes, matching the unknown solution against colours prepared from standard aluminium solutions; they claim that the error ought not to exceed 10 per cent. Winter and Bird[4] give results obtained by using the method of Winter, Thrun and Bird,[5] and claim for them an accuracy within 5 per cent.; they used the Duboscq colorimeter. Beal (and others),[6] and G. J. Cox (and others)[7] used a similar method, but employed a permanent colour standard in place of prepared aluminium standards.

During the last six years we have had an opportunity of perfecting and standardising the technique now to be described, for, from a detailed study of the effect of various factors upon the stability, intensity and quantitative colour character of the aluminium lake produced by aurin tricarboxylic acid, it became clear to us that the procedure must be definitely controlled in order to obtain assured sensitivity and quantitative results. From a study of these factors we have accordingly developed a method which, followed strictly, gives the desired accuracy.

Modifications and Standardisations of the Processes

(*a*) *Stability of the Lake.*—We have found the addition of glycerol, as used by Atack,[1] in the alizarin "S" method, to be satisfactory for this purpose.

(*b*) *Colour Standards.*—For very small amounts of aluminium the colour obtained is orange, and as larger amounts are taken the amount of red colour increases and the yellow colour decreases until the colour is pure red. For still larger amounts the colour is bright bluish-red, the red, blue and brightness increasing as the amount of aluminium is increased. The importance of these colour changes has not been sufficiently realised, for it is apparent that a colorimeter of the Duboscq type cannot satisfactorily be used for the colour measurement unless the amounts of aluminium in the solutions to be compared are practically identical; the same objection applies to the use of a permanent colour standard. The use of Nessler tubes is a cumbersome process, involving the preparation of a range of standards for every determination.

We have found that these difficulties are overcome by the use of the Lovibond tintometer. The method which we have adopted is to measure the tintometer colour values for solutions containing known amounts of aluminium, and to plot the red units on a graph which can then be used for determining the unknown aluminium content of other solutions. The direct comparison of one solution with another is thus avoided.

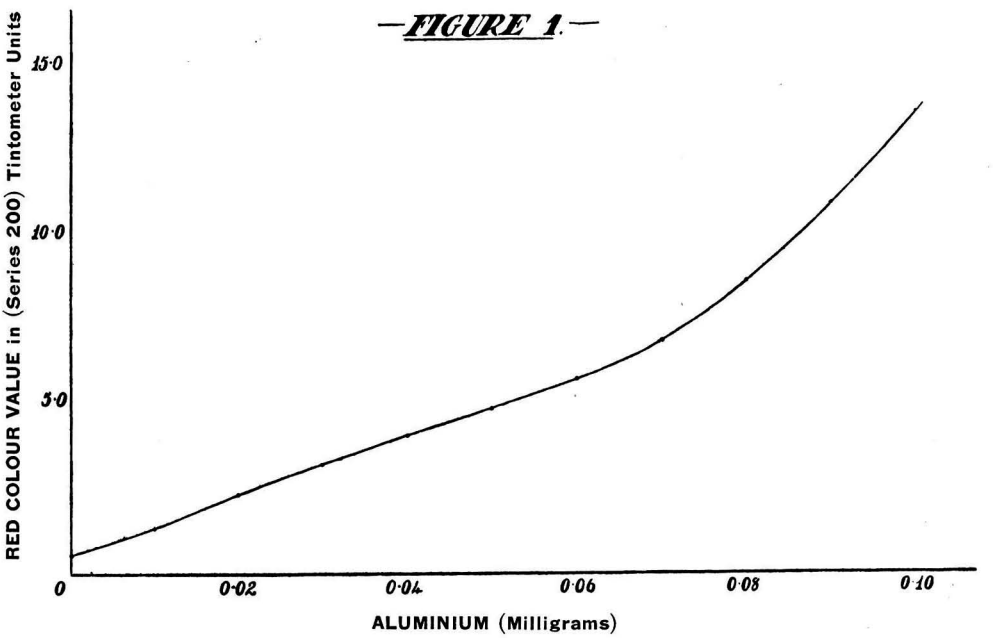
As will be seen from Table I, and from the graph in Figure 1, the red colour value (Series No. 200) is directly proportional to the amount of aluminium up to 0·06 mgrm. The yellow colour is obviously of no value as a factor for the determination.

TABLE I

Mgrms. of aluminium	Colour values of the solution in tintometer units		
	Red (No. 200)	Yellow (No. 510)	Blue (No. 1180)
nil	0·55	0·80	—
0·01	1·35	0·70	—
0·02	2·35	0·55	—
0·03	3·20	0·40	—
0·04	4·10	0·30	—
0·05	4·90	0·25	—
0·06	5·80	0·15	—
0·07	6·95	0·10	—
0·08	8·70	—	—
0·09	11·00	—	0·10
0·10	13·70	—	0·40

The red colour values for known amounts of aluminium are plotted in the graph in Fig. No. 1. The aluminium-content of a solution can, therefore, be calculated from a simple formula, *viz.* (R–0·55) × 11·5 × 10^{-6} grms., where R is the red colour value of the solution in Lovibond units (Series No. 200), provided that R does not exceed 6 units.

—*FIGURE 1.*—



(*c*) *Preparation of Standard Aluminium Solutions.*—A series of standard aluminium solutions was prepared, using potassium alum, ammonium alum, and metallic aluminium, but it was found impossible to obtain concordant colour values for the different solutions. The difficulty was overcome by adding a small

amount of hydrochloric acid to the standard solutions, and, when this was done, concordant results were obtained.

A somewhat similar fact is recorded by Pope,[8] who, in a recent paper, suggests that the loss of aluminium may be due to adsorption on the surface of the glass apparatus.

(*d*) *Standardisation of Conditions of Lake Formation.*—It is necessary to adopt a standard technique with regard to temperature and time, as well as the amounts of the reagents, since the final colour value of the solution is dependent on these factors, as well as on the amount of aluminium present. These points have been investigated by Yoe and Hill,[9] and by Winter, Thrun and Bird.[5] It has been shown that the lake formation is slow at ordinary temperatures, but that at about 100° C. it is rapid and complete. The colour fades after the addition of the ammonia and ammonium carbonate reagent, and the quantity added affects the actual colour-value of the solution, and also the rate of fading.

We have investigated the effect of these factors, and have found that uniformity of results can definitely be assured by heating the solution during lake-formation in a boiling water-bath for five minutes, and by subsequently cooling the solution in ice-cold water before the addition of the ammonium-hydroxide-carbonate solution. The colour is then measured in the Lovibond tintometer exactly five minutes after neutralisation with the ammonium-hydroxide-carbonate solution.

Winter, Thrun and Bird[5] claim that the fading of the final solution can be obviated by adjusting its *p*H to 7·1 to 7·3 with ammonium carbonate. Such a solution contains an excess neither of ammonium carbonate nor of ammonium hydroxide, and, in our opinion, this procedure is undesirable, since it makes no provision for the presence of small amounts of other metals, *e.g.* calcium, which might interfere.

Recommended Procedure for the Determination of Aluminium.—The procedure adopted for preparing the colour graph from the standard aluminium solutions or for determining the unknown aluminium-content of a solution to be analysed is as follows:

(*a*) *Reagents.*—*Standard Aluminium Solutions.*—1·757 grms. A.R. potassium alum, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, is dissolved in water containing 25 c.c. of 5 *N* hydrochloric acid, and made up to 1,000 c.c. (1 c.c. = 0·0001 grm. aluminium). This solution is diluted 5 times to give a standard solution of which 1 c.c. = 0·02 mgrm. aluminium.

Hydrochloric Acid.—5 *N*.

Ammonium Acetate.—5 *N*. A solution containing 386 grms. of A.R. salt per litre.

Aurin Tricarboxylic Acid Reagent.—Two grms. of aurin tricarboxylic acid are dissolved in water containing a slight excess of ammonia. The solution is boiled to expel the excess ammonia, and is then made up to 1 litre with distilled water.

Glycerol Solution.—A solution containing equal volumes of water and glycerol. This is more convenient to use than pure glycerol.

Ammonium Hydroxide-Carbonate Solution.—Equal volumes of 10 *N* ammonium hydroxide solution and of 2 *N* ammonium carbonate solution are mixed. This solution should be kept in a well-stoppered bottle, and examined occasionally to ensure that it has not deteriorated through evaporation.

(*b*) *Analytical Procedure.*—The following details must be strictly followed:—Five c.c. of a neutral solution containing the aluminium are placed in a 100-c.c. conical flask; exactly 2 c.c. of 5 *N* hydrochloric acid, 5 c.c. of 5 *N* ammonium acetate, 20 c.c. of 50 per cent. glycerol, and finally, exactly 5 c.c. of aurin tricarboxylic acid reagent are added. The contents of the flask are well mixed, and the flask is immersed in boiling water for 5 minutes, and then cooled in a mixture of ice and water for at least 5 minutes. The contents of the flask are washed into a 50-c.c. graduated flask containing exactly 3 c.c. of the ammonia and ammonium carbonate solution, mixing the solutions at the time. After making up to the mark with water and mixing thoroughly, the colour of the solution is measured in the $\frac{1}{2}$-inch cell in the Lovibond tintometer, exactly 5 minutes after the neutralisation with ammonia and ammonium carbonate solution.* Red slides of Series No. 200 are used.

II. Preparation of the Solution for the Determination of Aluminium from Food Materials.—We have found that a satisfactory procedure by which all the aluminium in the sample is obtained in solution ready for determination as in (I), is as follows:—Ten grms. of the material are destroyed in a silica flask with nitric and sulphuric acids until a colourless residue is obtained. After cooling, this is diluted with 50 c.c. of water, care being taken to ensure complete solution of the aluminium sulphate (this precaution is necessary, if relatively large amounts, *e.g.* 100 parts of aluminium per million, are present). A slight excess of ammonia is then added, and the solution is boiled until the vapours no longer smell of ammonia. This operation is the most important stage in the determination, and is the only point at which a serious error may be made. The excess of ammonia must be removed, otherwise an appreciable loss of aluminium will occur. On the other hand, if the boiling is unduly prolonged, the solution becomes definitely acid, and the precipitated aluminium is re-dissolved. When the operation is correctly carried out, the solution is neutral to methyl orange. After boiling off the ammonia, the solution is filtered through a 9 cm. No. 41 Whatman filter, and washed with 10 c.c. of cold water. The filtrate should be tested with methyl orange.

The precipitate is dissolved from the filter paper with 15 c.c. of hot dilute hydrochloric acid (5 c.c. 5 *N* acid + 10 c.c. water), which is poured slowly, drop by drop, around the upper part of the filter paper, and the latter is then similarly washed with 10 c.c. of hot water. The acid and the washings are collected in the silica flask, and 10 c.c. of 5 *N* sodium hydroxide solution are then added. After boiling and cooling, the solution is filtered through a 9 cm. No. 54 Whatman paper, and the filtrate is collected in a 50-c.c. graduated flask. The silica flask and the

* It will be noticed that the quantities used by us are somewhat different from those suggested by Hammett and Sottery. However, the essential feature of the test is the same, namely, the formation of the aluminium lake in an acetic acid and ammonium acetate buffer solution. The hydrogen-ion concentration of the above solution, and also that of the solution which would be obtained by adhering to the instructions of Hammett and Sottery, were measured. In both cases the *p*H was found to be 4·8.

filter paper are washed with cold water (15–20 c.c.) and, after cooling, the contents of the flask are made up to the 50 c.c. mark with water.

An aliquot portion of this solution is taken for the aluminium determination and placed in a 100 c.c. conical flask. For an aluminium content between 5 and 50 parts per million of foodstuff, 5 c.c. is a suitable aliquot portion. (If a smaller aliquot part is taken, the volume must be made up to 5 c.c. with water.) Sufficient 5 *N* hydrochloric acid is added to neutralise the caustic soda present (*i.e.* one-tenth of the aliquot volume), and then 2 c.c. in excess. The colour value of the solution is then determined by the standard method already described.

Using the red colour value thus obtained, the amount of aluminium in the aliquot volume can be read from the graph, and the aluminium content of the food can be calculated, after correcting for the aluminium present in the reagents.

The necessity for removing the excess of ammonia was not at first appreciated; in fact a slight excess was purposely allowed to remain, and faintly ammoniacal wash water was used. The erratic results which were obtained are illustrated in the following table.

TABLE II

	Aluminium added Parts per million	Aluminium found Parts per million
Jam	24	22
	50	46
	100	73
Milk	15	2
	18	10
	25	6
	30	11
	30	21

In the case of the third determination on milk, the filtrate from the ammonia precipitation was boiled to expel the small amount of ammonia which remained, and was again filtered. The amount of aluminium recovered was equivalent to 19·5 parts per million, which made a total of 25·5 parts per million.

The effect of excessive boiling, beyond the point at which the excess of ammonia is expelled, is illustrated by the following determinations. The sample used was fruit pulp.

Aluminium added Parts per million	Aluminium found Parts per million
27	19
33	20·5

Our experience offers an explanation of the statements in the literature that it is not possible completely to precipitate small amounts of aluminium by a simple ammonia precipitation, *e.g.* Myers, Mull and Morrison.[3] It seems probable that aluminium hydroxide is slightly soluble in ammoniacal solutions, and this is in accord with the work of Hatfield and others,[10] who have shown that the minimum solubility zone of aluminium hydroxide is over the range *p*H 5·7 to 7·3 for ordinary bicarbonate drinking waters.

TYPICAL RESULTS OBTAINED BY THIS METHOD.—The results given in Table III have been obtained by the above method, known amounts of aluminium having been added to 10 grms. of food. A control determination was carried out on 10 grms. of the food *plus* reagents.

TABLE III

Material	Aluminium added Parts per million	Aluminium found Parts per million
Fruit pulp	30	30
Milk	50	51
	100	100
Jam	50	50
	100	100
Tomato purée	2	3
	10	10·5
	20	21

The possible interference with the accuracy of the method by other metals was investigated.

Various metallic salts, etc., together with known amounts of aluminium solution were added to samples of food, and the aluminium determined according to the procedure described. Results which are given in Table IV indicate that these added substances have not in any way interfered with the accuracy of the results for the amount of aluminium.

The procedure which has been outlined is that which we consider most convenient for ordinary use. If, instead of 20 c.c. of 50 per cent. glycerol, 10 c.c. of pure glycerol be used in the colour formation, then an aliquot part of 15 c.c. may be taken, and the method is capable of detecting and roughly estimating 2 or 3 parts per million in 10 grms. of food.

If the method is further modified so that the total filtrate from the sodium hydroxide precipitation is taken for the colorimetric determination, it seems probable that very small amounts could be detected and estimated, especially if more than 10 grms. of food be taken.

We have made some preliminary determinations by such a modified method, and we have been able to detect the presence of 0·2 part per million of aluminium in 20 grms. of food. This problem, however, needs further investigation, and we hope that it will form the subject of a subsequent communication.

THE ALUMINIUM-CONTENT OF FOOD COOKED IN ALUMINIUM VESSELS.—We have carried out a few experiments in order to give some indication of the amounts of aluminium which are liable to be present in foodstuffs which have been cooked in an aluminium saucepan. No attempt was made to carry out accurate corrosion tests, and ordinary culinary practice was followed.

TABLE IV

Foodstuff	Salts added equivalent to Parts per million	Aluminium added Parts per million	Aluminium found Parts per million
Fruit pulp ..	100 of copper	45	43
		10	12
	100 ,, lead	40	41·5
		10	11·5
	100 ,, tin	60	61
		59	57·5
		16	16
	200 ,, tin	130	130·5
Jam	100 ,, iron	33	34·5*
		3	2*
Fruit pulp ..	1000 ,, iron	66	64
		20	19
Milk	50 ,, zinc	98	96*
		19·5	18·5*
		1	1*
Fruit pulp ..	100 ,, zinc	38	38·5
		14	15·5
	100 ,, manganese	60	60·5
		12	13
Soup	100 ,, nickel	77	78*
		17	16·5*
		7	7·5*
Fruit pulp ..	1 per cent. of P_2O_5	35	34·5
	1000 p.p.m. of calcium + 1 per cent. of P_2O_5	50	53
		10	11
	1000 p.p.m. of manganese	10	9·5
	1000 p.p.m. of manganese + 1 per cent. of P_2O_5	50	47·5
Tomato purée ..	Boric acid (200 p.p.m.)	21	21·5*
		3	3*
		1	1*

* It is of interest to note that in the case of the determinations marked with an asterisk the workers concerned had no idea of the amounts of aluminium present, or of the other added metals.

Tap Water.—London tap water was boiled for about half-a-minute, and then allowed to remain in the saucepan overnight.

	Aluminium-content
Before boiling	0·3 parts per million.
After boiling	2 ,, ,,
After standing overnight	3·5 ,, ,,

Milk.—An experiment similar to that with tap water was carried out, using fresh milk.

	Aluminium-content
Before boiling	0·4 parts per million.
After boiling	0·6 ,, ,,
After standing overnight	2·5 ,, ,,

Apples.—After peeling and coring, the apples were cooked for half-an-hour, with a little sugar and water.

	Aluminium-content
Before cooking	2 parts per million.
After cooking	14 ,, ,,

Tomato Soup.—The soup was prepared from peeled tomatoes and soup stock, and was cooked for half-an-hour.

	Aluminium-content
Before cooking	1 part per million.
After cooking	10 parts ,, ,,

Potatoes.—The potatoes were peeled and washed, and cooked in water containing 0·5 per cent. of salt for half-an-hour.

	Aluminium-content
Before cooking	2 parts per million.
After cooking	6 ,, ,,

Cabbage.—After washing, the cabbage was cooked for half-an-hour in water containing 0·02 per cent. of sodium bicarbonate and 0·25 per cent. of salt.

	Aluminium-content
Before cooking	8·5 parts per million.
After cooking	9·5 ,, ,,

Notes on the Determination of Aluminium in Food by a Spectrographic Method

Introduction.—In addition to the colorimetric method described above, it was considered that the specific and positive evidence offered by the spectrographic method was of importance when dealing with small amounts of aluminium.

The work of previous investigators on the determination of aluminium in biological material was reviewed from the original work of Hartley[11] up to the present time. Faced with the special problem of the determination of aluminium in very diverse products with no foreknowledge of the amount of aluminium which might be present or of other mineral constituents, we have attempted to evolve from this published work and our own experience a suitable method.

Experimental Procedure.—The method of wet destruction with sulphuric and nitric acids was employed, using 5 to 10 grms. of the material, as ashing may lead to losses of metals present in small quantities. The aluminium is precipitated from the resulting sulphuric acid solution (after dilution) with ammonia in the presence of ammonium acetate, filtered on No. 41 Whatman paper, dissolved in 5 *N* hydrochloric acid, and concentrated to 1 c.c. A portion of this is then evaporated in a trough cut in the electrode, and the residue is submitted to spark

excitation. Copper electrodes were used and cleaned between exposures by soaking in 5 *N* hydrochloric acid, which was found to remove all traces of previous residues. The usual precautions were taken in the photographic procedure to ensure uniformity.

A blank was taken on the full amount of the reagents, the same procedure being followed as with a determination. The amount of aluminium found in the blank was $0{\cdot}4 \times 10^{-5}$ grm. A series of standards of various amounts of aluminium was prepared by passing them through exactly the same process of destruction, precipitation and concentration on the electrodes.

The determination was concluded by comparing the intensities of the experimental plates with the standards. Judgment by the eye alone was used, aided by a spacing of the spectra so that by super-imposing the plates any experimental spectrum could be brought between any two standards.

It was attempted in devising the technique either to minimise as far as possible the range of variations, or to conduct the analysis in such a way as to make the same variation occur in both the sample and standard spectra. It is still evident, however, that the greatest source of variation is in the variable nature of the spark, and this constitutes the source of the greatest inaccuracy.

Typical results are as follows:

Substance	Salts added Equivalent to parts per million of aluminium	Total aluminium determined Parts per million	Net aluminium determined Parts per million	Other metals, etc., Parts per million
Milk	0·0	0·3	Blank	
	0·2	0·2	—	
	0·9	1·2	0·9	
	1·3	0·9	0·6	
	0·0	0·5	Blank	
	0·7	1·1	0·6	
	1·1	1·75	1·25	
	1·5	2·0	1·5	
				Zinc
	19·6	13·0	13·0	50
	98·0	85·0	85·0	,,
	0·0	0·0	Blank	,,
	0·98	1·0	1·0	,,
				Boric acid
Purée ..	21·0	25·0	24·0	50
	0·0	1·0	Blank	,,
	1·0	Nil	—	,,
	3·0	3·5	2·5	,,
				Iron
Jam ..	3·0	1·5	1·5	100
	32·0	21·0	21·0	,,
				Nickel
Soup ..	0·0	2·5	Blank	100
	15·0	10·0	7·5	,,
	16·0	8·0	5·5	,,
	26·0	15·0	12·5	,,

The above table shows the results from a series of samples which had been prepared by the addition of aluminium and other salts by an independent worker in the laboratories.

CONCLUSION.—A method of concentrating the aluminium-content of a biological material on to an electrode has been devised so that no possible loss occurs. The spectrum is then excited by a condensed spark discharge modified to remove air lines, as far as possible, and a quartz spectrograph is employed to photograph the spectrum. The plate is developed under standard conditions, and then compared with sets of standards on plates prepared under precisely similar conditions.

The results show that aluminium is detectable down to 1×10^{-6} grm. or 0·1 part per million on a 10 grm. sample, and the intensities of the lines at 3944 and 3961·5A can be used to judge the amount present up to 2×10^{-5} grm.

The accuracy of the determinations does not compare favourably with that of the chemical method described above, but is sufficient for the purpose, namely, to confirm specifically that the contamination is due to aluminium, and that the amount found is of the right order.

The authors desire to thank Messrs. J. Lyons & Co., Ltd., in whose laboratory this work was carried out, for permission to publish; Miss M. Wilcox, B.Sc., Mr. A. N. Ainsworth, B.Sc., A.I.C., for assistance in the practical work; and Mr. E. B. Hughes, M.Sc., F.I.C., for helpful criticism.

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The Physiological Action of Aluminium*

BY J. H. BURN, M.A., M.D.

(*Director of the Pharmacological Laboratory, Pharmaceutical Society of Great Britain*)

(*Read at the Meeting, June* 1, 1932)

INTEREST in the physiological action of aluminium and of aluminium compounds has been aroused, not only because of the use of aluminium for cooking vessels, but also because of the use of alum in baking powder. Little work has been done in this country, but much has been done in Germany and in the United States. The first work of importance was that of Siem, who published a dissertation in

* The following account is an abbreviation of a review of the published information respecting the toxicity of aluminium and its compounds which I have written at the request of the British Non-ferrous Metals Research Association.

1886, giving an account of work done under Prof. Hans Horst Meyer in Marburg. Siem fed cats on sodium aluminium tartrate, giving daily doses corresponding with 0·1 grm. of alumina for four weeks. He observed an initial diarrhoea, but otherwise no effect of any kind. This dose given to an animal with a body weight of 2·5 kilos. corresponds with a dose of 2·5 grms. or 37 grains of alumina a day for a man weighing ten stone.

When injections were made under the skin, Siem found that the lethal dose for rabbits, cats and dogs ranged from 0·25 to 0·3 grm. per kilo.; no matter how large a dose was injected, death did not occur until after seven days. Siem's work, therefore, although undertaken nearly fifty years ago, established from the first what has, in the main, been confirmed by all subsequent workers, namely, that the daily consumption of relatively large amounts of aluminium in the food has no ill effects, though when aluminium compounds are injected under the skin they will cause death, provided the amount given is large enough.

To those who may think that, if a substance is toxic when injected, it must also be toxic when taken by mouth, the effects of magnesium compounds may be pointed out; magnesium and aluminium are related elements. The compounds of magnesium are harmless by mouth; we give magnesia to children as the most harmless of all laxatives, and many of them take it daily for years. Yet, introduced under the skin, magnesium compounds are toxic; a dose of crystalline magnesium sulphate from 1·0–2·0 grms. per kilo. (corresponding with about 0·1–0·2 grm. of magnesium per kilo.) produces immediate narcosis, and death after a short interval, in mice and in rabbits.

The toxic action of magnesium when injected is due to its narcotic action on the nervous system; death follows because of paralysis of the respiratory centre. To what is the toxic action of aluminium due? This has been studied by Siebert and Wells. These workers carried out a lengthy investigation in which they used rabbits, and in which they determined the effect of aluminium compounds after intravenous injection. They found that when 0·04 grm., or about two-thirds of a grain, of alum was injected every day into the ear vein of a rabbit (weighing about 2·5 kilos.), after two to three weeks the rabbit became anaemic. The percentage of haemoglobin, always decreased, and the number of red corpuscles finally declined in all the rabbits except one. The same decrease in the percentage of haemoglobin was observed in rabbits which received daily injections of 0·01 grm. of aluminium chloride. When these rabbits were killed and examined, the only pathological changes which the authors could attribute with certainty to the injections were in the spleen, where they found pigmentation, thrombosis, necrosis and fibrosis; the spleen changes were severe. There were also changes in the kidneys which were "presumably, truly an aluminium effect"; these were extensive vacuolation and granular degeneration of renal epithelium.

The physiological action of aluminium compounds, as indicated by the work quoted, is an action on the blood system, whereby the subject is rendered anaemic; this effect, however, is only observed when the aluminium compounds are injected, and not when they are given by mouth; by mouth they are without effect in ordinary amounts. It will be convenient to take this statement and consider how far it

requires modification in the light of some of the different investigations which have been made.

EFFECT OF ALUMINIUM ON GROWTH AND REPRODUCTION.—Perhaps the most sensitive test of the harmfulness of any constituent of the diet is the effect of the constituent upon the growth of young animals. If a harmful substance is added to the diet of growing animals, it is common to observe that even when the animal is not obviously out of health, its growth-rate declines. In 1928, McCollum, Rask and Becker described the effect of adding aluminium chloride, and also alum baking powder, to the diet of young growing rats, so that the diet contained about 0·07 per cent. of metallic aluminium. It was observed that the growth-rate, reproduction and general health of the groups of rats receiving the aluminium were exactly the same as those of the control animals.

In the same year a similar piece of work was published by Myers and Mull (1928), also upon the effect of adding aluminium to the diet of young rats. Rats fed on a uniform diet were given 0·002 grm. of aluminium per rat for at least one hundred days, and during the course of the work four generations of animals were raised and the fifth was weaned. Growth in both the control and aluminium-fed groups was above Donaldson's normal for males and for females. There was a slightly more rapid initial growth of the aluminium-fed stock. This work is important, because the effect of aluminium was so thoroughly examined in successive generations of animals; if a harmful action had been exerted, it could not have escaped detection. The examination of the effect on growth was a quantitative examination in which composite growth curves for the different groups of animals were compared.

These two series of experiments by McCollum and his collaborators and by Myers and Mull furnish very important evidence, sufficient, I think, to convince all workers on nutrition that aluminium in the diet in small amounts is entirely harmless. The evidence these experiments provide, that reproduction is not affected, is of value because of the opposite conclusion reached by a group of French workers, Schaeffer, Fontés, Le Breton, Oberling and Thivolle. Schaeffer and his colleagues published a paper in 1928 in which they described the damage produced in the stomach and small intestine of mice by feeding them with aluminium compounds; this was severe. In dogs, however, the feeding with aluminium salts had no such effect, though the authors described areas of congestion in the large intestine. There were, however, no control observations on animals which had received no aluminium, and areas of inflammation in the large intestine of dogs, particularly of dogs abroad, may be due to many causes. Schaeffer and his colleagues were most impressed by the effect of aluminium-feeding on reproduction in mice, and thought that in these experiments they had the best evidence of the danger of aluminium in the diet. One experiment was as follows:—They took four groups each with ten pairs of mice; the first group was fed on bread with yeast, and in four months had 328 offspring; the second group was fed on the same diet, but had a larger percentage of a salt mixture and produced 310 offspring; a third group was fed on bread made with alum-phosphate baking powder, so that the diet contained 4·4 per cent. of aluminium: this group had only 192 offspring;

the fourth group had the same diet as the third, but only 1·3 per cent. of aluminium: it produced 244 individuals. The authors say "these results are so outstanding as to need no comment. They can be explained by an elective specific action of the aluminium ion on the ovary."

The deduction that the aluminium ion has a specific action on the ovary is unwarranted by the evidence, and reveals a very uncritical attitude on the part of these workers. No details of the experiments are given, and had the work indicated the harmlessness of aluminium rather than the opposite, the work would have been disregarded. It has, however, been quoted by those who think that aluminium is harmful. Even if, for the sake of argument, the work is accepted as trustworthy, it merely shows that when so large an amount of aluminium salts is added to the diet as to raise the content of aluminium to 1·3 per cent., the reproduction is reduced from about 300 to 250. This is scarcely noteworthy. Raising the aluminium percentage to 4·4 reduced reproduction from 300 to 200. At the worst, the only conclusion is that relatively enormous amounts of aluminium salts in the diet do not do more than restrict reproduction, and, as shown by the more dependable and fully documented experiments of McCollum and of Myers, smaller amounts have no effect whatever.

THE ABSORPTION OF ALUMINIUM FROM THE ALIMENTARY CANAL.—Much work has been done on the absorption of aluminium salts from the stomach and intestines into the blood stream, the animals employed being either rats or dogs. The best papers are those of Myers and Morrison (1928) and of Underhill and Peterman (1929). The actual results do not appear to differ greatly, but Underhill and Peterman conclude from their experiments that aluminium is promptly absorbed in small quantities following a single administration of food to which it has been added. The figures in support of this conclusion are given in Table I, taken from their paper.

TABLE I

ALUMINIUM AS MGRMS. PER 100 GRMS. OF WET TISSUE

Procedure	No. of dogs	Liver	Bile	Kidney	Brain	Heart	Spleen	Thyroid
1 week starving ..	12	0·94	1·9	0·84	1·25	0·19	1·84	7·25
1 week meat and bread	12	0·66	1·86	1·12	1·45	0·18	2·01	5·5
Single feeding ..	15	0·6	2·5	0·76	1·64	0·26	2·16	5·3
1 week feeding ..	6	0·84	2·27	0·50	1·63	0·5	1·85	6·1
1 week control ..	2	0·44	2·02	0·75	1·31	0·147	2·45	10·4
1 month feeding ..	6	0·73	1·75	0·65	1·20	0·29	2·12	5·2
1 month control ..	2	0·67	1·40	0·65	1·15	0·18	1·82	4·0
3 months feeding ..	6	0·83	1·95	0·54	1·19	0·19	2·41	6·1
3 months control ..	2	0·74	1·44	0·58	1·28	0·07	2·11	3·8

The figures show that aluminium is present in the tissues of starving dogs, as well as in those of dogs fed on meat and bread containing no aluminium. After a single feeding with food containing aluminium, there was a slight rise in the aluminium-content of the bile, the brain, the heart and the spleen; the rise in all these tissues is so slight, however, that it is surprising to find the authors drawing the conclusion already stated; moreover, after feeding aluminium for a week, the

figures, except for the heart, are less than after a single feeding, so that it is even more puzzling that the authors should say "aluminium continues to be absorbed when aluminium-rich diets are fed for various periods of time."

The experiments of Myers and Morrison (1928) on the absorption from the alimentary tract were performed on dogs which received 0·23 and 1·55 grm. of aluminium daily for three months. These were compared with normal control dogs. There was almost no difference in the aluminium-content of the spleen, kidney and heart, but in the liver the aluminium-fed dogs had an average of 0·27 mgrm. of aluminium per 100 grms. of tissue, against an average of 0·15 mgrm. of aluminium per 100 grms. of tissue in the control dogs. When 5 mgrms. of aluminium were injected daily into two dogs for two weeks, an increase in the aluminium-content of the tissues was still evident as long as thirty-four days after the administration was discontinued, indicating that when aluminium is present in the tissues it is only slowly excreted.

These results fully support the conclusion that only traces of aluminium compounds are absorbed from the intestines.

Experiments on Man.—It is not often that a medical problem can be put to the final and conclusive test of experiment on the human subject, and in the few cases in which it can, the result of the experiment is generally accepted as closing discussion once and for all. The agitation against the use of alum baking powder in the United States during the years 1911–1914 led to a formal investigation by the Department of Agriculture. The President of Johns Hopkins University was chosen as Chairman of a board, to which some of the most prominent American workers on nutrition were appointed. The board instituted three independent sets of experiments which were carried out on university students in different universities. The numbers of men used were twelve, six and eight, respectively, and these were given daily amounts of alum for a period of about six months, the daily amounts varying from 0·23 grm. to 10·0 grms. The food was all carefully measured and weighed, the excretions of urine and faeces were collected and analysed, daily records of body weight, temperature, respiration and pulse were kept for each man, and notes were made of any unusual symptoms. The results of the experiments in the three different universities were the same, and the conclusion that aluminium compounds present in small quantities in the food are harmless, was drawn by all three investigators. They state that amounts of aluminium up to 75 mgrms. a day are quite harmless; amounts up to 200 mgrms. may provoke mild catharsis, that is some looseness of the bowels; amounts up to 1 grm. per day usually produce catharsis.

It is obvious that this report of the United States Department of Agriculture is of great significance. Twenty-six human beings were deliberately fed with aluminium compounds for a period of six months, and careful observations of their health were made during this time. It was shown that, without exception, the subjects were entirely unaffected, except that large doses of aluminium salts caused mild catharsis.

The Amount of Aluminium coming from Cooking Utensils.—The amount of aluminium coming from cooking utensils has been determined by different observers, and the most complete data I have found are those given by Massatch

(1929). He determined the amount of aluminium in the ash of a series of dishes such as scrambled eggs and bacon, cabbage, meat stew, soup, cakes, stewed apples, and cocoa. From the weights of the ingredients taken it is possible to calculate how much aluminium an individual would consume per day if he ate all these dishes. The result is given in Table II.

TABLE II

	Al_2O_3 Mgrms.
From scrambled eggs and bacon	0·06
From cocoa	0·6
From cabbage cooked in vinegar ..	5·5
From goulash	0·25
From bouillon with beef	0·45
From cakes	0·3
From apple sauce	6·0
Total	13·16

The total amount of 13 mgrms. of alumina corresponds to approximately one-tenth of a grain of aluminium. The small quantities of aluminium which the report of the United States Department of Agriculture states have no effect whatever, are up to 1·16 grains daily, or more than ten times as much as Massatch's figures indicate will come from aluminium utensils. This evidence should be sufficient to dispel any doubt remaining after the results obtained in the rat experiments have been fully considered.

CLINICAL OBSERVATIONS.—It remains to deal with certain clinical observations which have recently been made by various medical men. A pamphlet has been printed by Dr. Cooper and distributed among the medical profession. Dr. Cooper's statements are that many patients suffering from indigestion and abdominal pains are relieved of their symptoms if they cease to use aluminium vessels for cooking their food. Recently there has been some correspondence in the *British Medical Journal* on this subject, and two other medical men have written supporting what Cooper has said, one of them stating that the idea of aluminium being harmful was introduced to him by Cooper. One reply, in the *British Medical Journal* of April 23rd, contains the following:—"The letter of Dr. Coram James in your issue of April 9th is explainable as an interesting example of faith-healing. Believing aluminium cooking utensils to be harmful, he convinces his patients that the financial loss entailed in scrapping their aluminium ware will be beneficial to their health, and it is."

It is a commonplace of medicine to-day that many new remedies produce wonderful effects at first, but that soon they lose their efficacy; doctors like to get hold of these new remedies quickly to use them "while they still work." The explanation is that the new remedies cure by a psychological effect which ceases when the remedies are no longer new.

I, myself, have no doubt whatever that all the relief of pain which attends the discontinuance of aluminium cooking vessels is due to psychological forces. My own conviction, however, and the similar conviction of others, will not shake

the opinions of those who think with Dr. Cooper; nor are they moved by experiments on animals.

In conclusion, there is one experiment which I think might be organised to answer such a letter as that in the *British Medical Journal* of April 16th from Dr. Alexander Francis. Dr. Francis says that he himself and six of his patients have got relief from abdominal pain by discontinuing the use of aluminium vessels. It is remotely conceivable that this is not a psychological effect, and that some people may be "anaphylactic to aluminium," as Dr. Francis expresses it. Why not test the matter? Let a number of these patients who imagine themselves sensitive to aluminium stay for some days in a hotel or house where it is arranged that they shall be given alternately food cooked in aluminium vessels and food cooked in other ware, without the patients knowing when the aluminium ware is used and when the other. The experiment would have to be arranged with care, but, if this were done, a clear answer might be obtained whether the aluminium ware did or did not give rise to symptoms in these patients, when psychological effects were excluded.

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DISCUSSION

The PRESIDENT thought that the paper by Dr. Lampitt and Mr. Sylvester had fulfilled a long-felt want. It seemed somewhat unfortunate that the American investigators had published rather lengthy lists of determinations of small amounts of aluminium in foods without mentioning how the results were obtained. One felt, perhaps, that the information lost a considerable amount of value because of this fact. Aluminium was not an easy element to determine. It had a characteristic—it formed an insoluble precipitate in the presence of ammonia, but there were two colour reactions, the one already described, and one which, he believed, Dr. Monier-Williams was going to mention later. The author of the last paper had mentioned the presence of alum in baking powder. So far as the President was aware, in this country this substance had disappeared from baking powder many years ago. He had no knowledge of its re-appearance. So far as the action of alkalis and acids on modern aluminium was concerned, he had had little experience, but some 20 or 25 years ago he had made determinations on the aluminium taken up by dilute acids and alkalis, and had been surprised at the extraordinary amounts taken up both by them and by common salt. They had had put before them that evening figures with regard to the aluminium taken into solution by weak salts, but he wondered whether the observer had taken into account the aluminium which was so often held loosely on the surface of the vessel after use. Not only did aluminium go into solution, but a considerable quantity was often loosened and very easily dissolved in any subsequent operation. He queried whether the metal determined was the metal both in solution and in suspension; also whether notice had been taken of the aluminium attacked. A result obtained after the action of a substance on clean aluminium might differ greatly from the result obtained by the action of the same substance on aluminium previously used and attacked as suggested. Dr. Burn had given a very fair resumé of the physiological effects of aluminium. He supposed that it was essential that this subject should be discussed, because scares had occurred both in Switzerland and in America, and therefore somebody certainly should be called upon to express views so that not only medical men, but also they, as Public Analysts, should have some idea as to the importance of the presence of small quantities of aluminium in food.

Dr. A. G. C. GWYER said that it had been his experience that aluminium was an element which did present difficulties in determination, and that these difficulties were always much

greater when the analyst was not daily analysing aluminium. A statement had, for example, been made quite recently that milk exercised a very considerable solvent action upon aluminium, and, as he had always regarded milk as being without action, he had put in hand a series of experiments with the view to testing the truth of the statement. As was well known, the most common foodstuffs contained calcium, and it was therefore to the separation of aluminium and calcium that attention was directed. Separation might be effected in one of two ways: either the calcium could be removed and the aluminium determined in the filtrate, or the aluminium could be directly precipitated under conditions which ensured that the whole of the calcium present remained in solution. A possible precipitant was hydroxyquinoline, but this had not been found satisfactory for determining small amounts of aluminium in the presence of large amounts of calcium, whereas, on the other hand, the phosphate method had been found to work well, provided certain precautions were taken. Here Dr. Gwyer described the method in detail, emphasising that the *p*H value must be adjusted to between 4·5 and 4·0 in order to effect a complete separation. A similar conclusion had been reached by Patten and Winter, except that they had placed the upper limit at 5·3, which was, in his (Dr. Gwyer's) opinion, too high. Having decided upon the best method to follow, Dr. Gwyer had next carried out tests in which fresh milk was boiled in both new pans taken from stock and in an old pan, which had been in continuous use for over 12 months. In this case 250 c.c. of fresh milk were brought to the boiling point, boiled for 2 minutes, evaporated to dryness, and ashed, the acidity being adjusted to between *p*H 4·0 and 4·5 by the addition of acetic acid and sodium acetate. The precipitate was finally weighed as aluminium phosphate. Under the conditions described, the weight so obtained was 0·0002 grm., a value which was identical with that of the blank, and the conclusion reached, therefore, was that the milk had not dissolved any aluminium. The extreme importance of keeping the *p*H below 4·5 was demonstrated by an experiment upon a solution which contained a known small quantity of aluminium in the presence of a relatively large amount of calcium, the *p*H being purposely adjusted to 4·9. In this case the precipitate which was weighed consisted mainly of calcium phosphate, although it contained all the small quantity of aluminium present. With such a high degree of acidity it might have been supposed that the precipitate would have consisted of aluminium phosphate, and had the amount been calculated on this assumption, the aluminium present would have been returned as 120 grains per gallon, whereas the fact was that the aluminium-content was well under one grain per gallon.

Professor C. K. TINKLER said that they knew that some quantities were taken up where aluminium cooking vessels were used, and they knew, thanks to Dr. Lampitt and Mr. Sylvester, that it was possible to determine with very great accuracy these quantities. He was very interested to see that the amount taken up by milk was so small. Miss Masters and he had found, some years ago, that there was a definite protective action by colloids. He was particularly interested in Dr. Burn's paper, because it was necessary that the views of physiologists should be obtained on such a question as whether there was danger in using aluminium cooking vessels, and analysts were often asked such questions. People had written to him asking whether there was any danger in this. He told them that he did not think that, so far, any case had been made out against the use of such vessels, but he thought it unwise to store acid foods in aluminium containers longer than was necessary. He had referred the matter to his physiological colleague, who said that his rats which fed from aluminium containers in which food was kept for some time appeared to take no harm and were very healthy, although they must take up large quantities of aluminium. Of course, of this argument it might be said, as had been said before, "All men are not rats and only a few are guinea-pigs."

Dr. E. B. VERNEY said that in a cursory glance through the literature of the subject, two papers had attracted his attention. One was by Schmidt and Hoagland, who were working, he believed, for the Referee Board of the U.S. Department of Agriculture. They had fed men on foods containing aluminium. In one series of men as much as 300 mgrms. of aluminium was given per day for 70 days in succession, and 99·9 per cent. of the aluminium given was recovered from the stools. The second series was fed with dosages up to 500 mgrms. a day for 118 days, and there was almost an equally good recovery rate. An amount of 500 mgrms. per day per man would correspond with 50 kilos. of tomatoes per day, according to Mr. Sylvester's figures. It seemed perfectly clear that aluminium given by the mouth was a non-toxic substance to man.

The other paper was by Bertrand and Serbescu, published in the *Bull. Soc. de Chimie biologique* last year. These authors investigated the toxicity of aluminium, comparing it with iron and nickel, by means of injections of the sulphates into guinea pigs, determining the length of time which the animals survived after a large dose. Those injected with equivalent doses of copper and nickel died within an hour; those which were injected with zinc died within three hours, and those which were injected with iron or aluminium sulphate survived eight hours. They concluded that when the sulphates of these metals were injected subcutaneously, aluminium was no more toxic than iron.

In conclusion, even if it were proved that cases of super-sensitivity to small amounts of aluminium actually did occur, he did not consider that this would be any reason at all for forbidding the use or manufacture of aluminium ware. One could not legislate for people with idiosyncrasies; if we did, the use of most drugs would be prohibited—a sufficiently appalling thought for the medical profession.

Sir WILLIAM WILLCOX said that it was always difficult to prove a negative, and that was rather the difficulty in which they were placed that evening. He had looked up certain forensic books and works on toxicology, and had not found aluminium, even in the index. Under "potassium" he had found "alum," and there was one case recorded in which a baby had died after taking several teaspoonsful of alum. If it had had several teaspoonsful of sand possibly the same thing would have happened. There was really no toxicological evidence that aluminium was poisonous. Most of the speakers that evening had made it clear that if aluminium was taken by the mouth it was not absorbed to any appreciable extent. The proof that aluminium was not absorbed was that such very minute quantities got into the blood, even when large doses were taken. Dr. Burn had quoted a paper in which it was shown that 99 per cent. of aluminium was recovered in the stools, after it had been administered by the mouth, which was a further demonstration of this point. The question of injections under the skin was not really under consideration. Many harmless foods, such as milk or beefsteak, would probably kill if injected under the skin.

Referring to fashions in medicine, Sir William mentioned the use of the term "allergical." This really applied to organic substances, and one could practically rule out the question of idiopathic idiosyncrasy with regard to metals. He had been practising medicine for a long time, and had seen many thousands of cases of ordinary dyspepsia, but never one in which the symptoms had been caused by aluminium. He had studied carefully the records of the clinical cases cited in the pamphlet to which reference had been made, and several of them appeared to him to be obviously attributable to something else than aluminium. In one case the patient, who had a temperature frequently, probably had a chronic appendix. The symptoms subsided, as these conditions did subside (especially when associated with auto-suggestion), well for a few months. Was it likely that aluminium was as terribly toxic as the author of the pamphlet would have us believe? Aluminium was present everywhere, and people were bound to swallow a lot of it. It seemed inconceivable, therefore, that the slight amount from aluminium cooking vessels could have any toxic effect. It was difficult to keep pace with all the patent medicines, but four or five years ago there was one called "Alocol," which was the very latest for the treatment of dyspepsia, gastric ulcers, etc. It was aluminium hydroxide, and was given in doses of 1 grm. from three to six times a day. To-day the fashion was kaolin, which was aluminium silicate; it often contained more than the legal amount of arsenic, so that if aluminium was harmful, he was sure that kaolin must be.

At present the position, from all that could be learned from scientific experiment and chemistry, was that there was no ground for stating that aluminium, as derived from cooking utensils, was harmful, but let open minds be kept, for, as he had already said, it was very difficult to prove a negative. To the best of his knowledge, however, there was no evidence that aluminium was harmful.

Professor J. C. DRUMMOND said that it was not easy to get so clear a view as Dr. Burn had presented because of the conflicting nature of the evidence in the literature. It was, of course, a matter of very great difficulty to reach a decision on the toxic action, if any, of such substances as aluminium salts. If tests on small animals, such as rats, failed to give definite results, it was always possible to investigate their action on man. The experiments made by the U.S. Dept. of Public Health were, however, open to criticism, mainly on the grounds that the doses administered were fantastically large when compared with those which might be consumed under normal conditions. Largely on the basis of such experiments, the use of borates as preservatives was condemned. Nevertheless, it was well-known that the workers in the boric acid districts of Italy showed normal health in spite of constant absorption of comparatively large amounts. It was not acclimatisation, for new workers from other districts did not suffer on being brought into the boric acid areas. Similarly, there was no evidence that workers in daily contact with aluminium salts experienced any harmful effect.

Dr. R. SELIGMAN said that, speaking as one who must bear a great amount of responsibility for the use of aluminium in the preparation of foodstuffs in this country, he would like to say how much he appreciated the fact that this subject was being brought on to the platform of a scientific society. He would like to draw attention to the relation between the two papers. They had heard from Dr. Burn the "evidence in the case." They had heard that there was no evidence of the toxic effect of aluminium, but that was not quite enough for those intimately concerned in this matter. They felt that they must know more than that there was no evidence. Therefore it was only as a first step in the investigations which they planned that they asked the Non-Ferrous Metals Research Association to select some gentleman to review the existing evidence. That Dr. Burn had done, and the results he had given. But Sir William Willcox had pointed out that it was difficult, if not impossible, to prove a negative of that kind. It was precisely there that the value of such a paper as that of Dr. Lampitt and Mr. Sylvester came in. He might say that the Association's second step was to have been a research to establish some reliable method of estimating very small quantities of aluminium. Luckily, the Association had been saved that, and they now had one colorimetric and one spectroscopic method of determining these small amounts. Therefore, they had advanced two steps in a very short time.

The importance of Dr. Lampitt's work was here: It was a commonplace that aluminium was everywhere; it formed just on 15 per cent. of the weight of the globe, and it was said to be in waters and in foods, and since time immemorial cooking had been done in clay vessels. What they wanted to know was whether it was really present in the foods eaten every day, because, if it were so present, he could not see how the suggestion of the special susceptibility to aluminium poisoning of some people could possibly be true. Dr. Burn, in his paper, had referred to a statement of Dr. Francis in the *British Medical Journal*. Dr. Francis had said that he was so sensitive to the effects of aluminium that if he tasted food cooked in aluminium vessels (even if no method of analysis was able to show traces of the metal) he immediately diagnosed it by suffering severe abdominal pains. One must set against that such work as that of Mme. Lévy, at the Pasteur Institute, who examined 55 common vegetables for aluminium, and whose results compared closely with those of Dr. Lampitt and Mr. Sylvester. We now had the results obtained by a number of methods of analysis, all different, which all came to the same result—that practically in all these foods there were appreciable quantities of aluminium present. Dr. Gwyer had explained away a statement in the pamphlet, which had been referred to several times that evening, to the effect that milk cooked in an aluminium saucepan dissolved 140 grains of metal per gallon in a few minutes. That statement struck him as amazing; he did not know whether the meeting realised its implication. He calculated that it meant that 3 tons of dissolved aluminium were being supplied with the milk to Londoners every day.

On behalf of those working in this matter, he wished to say that they did not consider the book closed or the chapter ended as yet. They were most anxious to test by any means which came to their knowledge whether the metals used by them were toxic in any way. He could quite believe that modern statistical methods might reveal some physiological effect of aluminium, but it would not be open to any honest man, after that evening, to speak of aluminium as a strong irritant poison.

Dr. T. C. HUNT mentioned that he had had a few patients, who had been convinced that they were suffering from aluminium poisoning. There were three, in particular, all of whom had assured him that their symptoms had ceased from the moment they stopped taking food cooked in aluminium vessels. In his opinion, it was almost conclusive that such a sudden cessation of symptoms implied a psychological basis. Could it have been from absorption of aluminium, the symptoms must surely have ceased gradually and have died away as the metal was gradually excreted. One saw so often the effect, as had already been pointed out, of faith and suggestion, particularly in matters relating to digestion. One had not any sort of clinical condition that could be attributed to aluminium. He thought that a fuller investigation of the excretions of some of the patients who attributed their symptoms to aluminium was needed, and a set of test experiments, such as Dr. Burn had suggested, with and without aluminium in the food, would be very useful.

Dr. R. S. HUTTON, speaking as Director of the British Non-Ferrous Metals Research Association, which asked Dr. Burn to investigate this matter, asked if he might be allowed to thank the Society for the opportunity of bringing this question before it. Dr. Drummond had pointed out that there was always a great risk in questions of this sort of some interested body taking a particular side and fostering some action for or against some particular material. His own Association was so conglomerate that all rival metals came within its purview. This matter was referred to the Association, and on behalf of them he went to the very highest authorities. As a first step, they were advised to get an impartial review of all the literature, and Dr. Burn was mentioned as being able to give a perfectly independent review of the matter. As far as he knew, Dr. Burn knew and cared very little about aluminium at the time. They were prepared and anxious, not only to make a review of the subject, but actually to put in hand any clinical or other research which might throw light on the subject. Their present opinion was that there was very little more to be done after this review, but they would be only too ready to consider any suggestions put before them for further research or study which would be useful.

Mr. H. W. WEBB said that he might be able to contribute a few words on the analytical aspect of the subject. Two years ago he had published, in collaboration with Dr. Schoeller, a paper on the application of tannin to the precipitation of various earth-forming metals (ANALYST, 1929, **54**, 711). They were able to prove that the bulky tannin precipitates were very suitable for the determination of small quantities of thoria, zirconia, titania, and alumina. A previous separation from iron by means of ammonium sulphide was readily carried out in ammoniacal tartrate solution, the filtrate from the ferrous sulphide being faintly acidified with acetic acid, boiled, and the aluminium precipitated with tannin in presence of ammonium acetate.

As regards the precipitation of alumina in presence of phosphoric acid, they had obtained some precipitates in which no phosphoric acid could be detected by molybdate, but others contained small amounts. Even if the final alumina precipitate had to be corrected for a small phosphoric acid content, he believed that the method would be very convenient for the determination of the minute amounts of alumina encountered in foodstuffs. A quantity of alumina of the order of 0·5 mgrm. could easily be handled without the use of special micro-apparatus.

Dr. G. MONIER-WILLIAMS (in a written communication) said that, in his experience, the hydroxy-quinoline method of Berg was the most satisfactory for the determination of aluminium in foods. Iron and aluminium were precipitated together as phosphates from a solution of the sulphated ash, and the iron was subsequently separated as basic acetate. Aluminium was precipitated in the filtrate as the hydroxy-quinoline compound, which was filtered off and titrated with $N/10$ bromate-bromide solution. Five c.c. of this solution were equivalent to about one milligramme of aluminium.

The experimental work so far carried out in his laboratory indicated that most, if not all, of the aluminium reported to exist naturally in fruits and vegetables was due to dust and dirt on the surface. If the surface were thoroughly cleaned with soap and water before analysis, the amount of aluminium in the sample was reduced to vanishing point. Fruits and leaves with rough or sticky surfaces naturally retained dust, and therefore showed, on analysis, an appreciable amount of aluminium. Little or no evidence had so far been obtained that aluminium was a normal constituent of the ash of plants.

Dr. S. JUDD LEWIS referred to a paper which he had published on the determination of aluminium in blood and milk by the arc-method of quantitative spectrography (*Biochem. J.*, **1931, 25**, 2162; ANALYST, 1932, 324). In a considerable number of experiments he found usually no aluminium in normal blood, but the blood of subjects fed with one scone containing 94 mgrms. of aluminium once a day for any number of days up to 14, showed a fairly constant aluminium-content of about 1 part per 1,000,000 of blood; but in one case it increased greatly. The earliest time at which aluminium was observed in the blood was 4·5 hours after administration, but it was much more evident after 24 to 48 hours. It showed quite early in the milk, both in humans and in cows and goats. Cows were drenched with a dose of aluminium immediately after one milking, and it was found in the milk of the next milking. This was rather important in connection with the absorption of aluminium.

Mr. F. R. STEPHENS observed that nothing had been said about the consumption of aluminium in the presence of a certain amount of organic acid. His own personal experience was that it had a very definite effect if taken in considerable quantity. All the cases mentioned had related to more or less neutral solutions, but in a strongly acid solution, such as tartaric or acetic acid, would aluminium not have some physiological action?

Major STANLEY ELLIOTT said that in the Army alum had been used for many years for clarifying water, without any injurious effect on the troops. Moreover, the cavalry had used an aluminium water-bottle, in which was placed sodium bisulphate, giving the water a *p*H value of 3, and making it sterile. This water contained about a grain of aluminium per gallon, the amount, of course, depending on the period of contact, and the statistics did not show that the British trooper suffered from anaemia or gastric troubles to any greater extent than the rest of the Army which used the enamelled iron bottle.

With regard to Dr. Cooper's pamphlet, he had been asked by the Director of Hygiene to check the chemical results. He found that the figures in most cases were wrong; in the experiment on soup it was stated that about 300 grains of aluminium per gallon were found—this would give a life of only about 20 stews of soup to a 3-ounce pan. Everyone was aware that aluminium pans had been in use for years in ordinary houses. He had found practically no difference in the action of foods on so-called "cast" and "spun" aluminium pans, the former being the thick material, the latter the thin metal. The method used was that of Hammett and Sottery, slightly modified in a different way from Dr. Lampitt's method, and he found that it gave excellent results, but, as iron gave a purple colour which interfered seriously with the matching of the colours in the test, it was very necessary to get rid of the iron. The results he obtained by heating foods in aluminium vessels were similar to those obtained by Dr. Lampitt and Mr. Sylvester. As the whole point of Dr. Cooper's objections to aluminium lay in the lesions in the intestine supposedly caused by its passage, he would like to know whether Dr. Burn had noticed any damage to the intestines of animals subjected to the action of aluminium in their food.

With regard to the tolerance of metals by people, the arsenic eaters of the Tyrol had acquired a high degree of tolerance to this substance, and other metals could be tolerated in comparatively large amounts; was it possible that a tolerance to aluminium could be acquired by human beings?

Miss H. MASTERS said that they had heard a great deal about cooking utensils. She would suggest that, from the practical point of view, the question might be raised as to what materials likely to be less harmful should be used as an alternative to aluminium. The choice of materials which could be used for cooking utensils was limited, and it was not a case of being able to select one which would yield nothing at all, but of trying to select the one which was least likely to yield injurious products. She welcomed the discussion that evening because it had shown that there was very little possibility of any harm being caused by the use of aluminium cooking utensils.

Mr. L. J. ODLING enquired whether Mr. Sylvester had made any experiments with softened water, such as was so often used in households to-day for cooking purposes.

Dr. K. MACKENZIE said that he had made one or two physiological experiments in connection with the absorption of aluminium into blood. He had started on the basis of work of Underhill,

who had fed dogs with a certain amount of aluminium, and had found aluminium subsequently in the blood, but on attempting to repeat the experiment on rabbits no aluminium at all could be detected in most cases. He then injected aluminium into the blood, and subsequently examined the blood. He was rather surprised that it did not show any aluminium, seeing that aluminium sulphates or solutions rather acid in character were being used. It was found that at least 50 per cent. of the aluminium could be recovered from the liver of the animal. He then went on to use the neutral solutions (aluminium tartrate), and in that case, also, on injecting about 1 mgrm. in solution, most of the aluminium disappeared in a very short time—within about one hour—and again, about 50 per cent. was found in the liver. He could not get any higher recovery. Next he introduced aluminium into the intestine of the animal and examined the portal blood to see whether the aluminium was carried by that course. It seemed possible that if aluminium were inserted into the small intestine it might travel in the blood stream into the liver and possibly be deposited there. An animal was anaesthetised, and about 1 mgrm. of aluminium tartrate in 10 c.c. of physiological saline was introduced into the intestines. Samples of portal blood were taken at intervals of 30 minutes, 1 hour and 2 hours, and it was found that very little of this aluminium had travelled, and upon subsequent examination of the intestine at least 95 per cent. could be recovered. This still left, of course, a 5 per cent. margin, and there seemed little doubt that some aluminium was transported in this way, but its amount was very slight.

Mr. A. SCIVER asked if Dr. Burn had come across any information in the literature with regard to the effect of traces of aluminium on bacteria, because of the possible connection between physiological action and oligodynamic action. It had to be assumed that aluminium was normally present in foodstuffs, but he did just wonder whether the form in which it was present might not make a difference. He did not think it a fair assumption to make that, since aluminium was present and harmless in kaolin, it was necessarily harmless when present as an acid salt in, say, fruit juice.

Dr. H. J. STERN raised the question of the purity of the aluminium used. The purer the aluminium the less it would be dissolved. He thought it might be that some of the older work was done with aluminium of less purity than that used at present.

Mr. E. HINKS said that he trusted that nothing that had been said during the evening would be construed as offering justification for the intentional introduction of aluminium compounds into food, for instance, alum in bread. Alum baking powders had fallen into disuse in this country, and their re-introduction would have to be considered apart from the question of traces of aluminium derived from cooking utensils.

Mr. A. SAMSON said he was interested in the remarks of Dr. Stern in connection with the purity of aluminium cooking vessels as used for analytical tests. Speaking from a practical point of view, especially in the case of cooking meats containing 2 to 5 per cent. of salt, his experience had been that vessels purchased 5 or 6 years ago did not last long, but that those vessels purchased 2 or 3 years ago were standing up much better. The salt seemed to have a very marked effect on aluminium vessels. Perhaps Dr. Seligman could say whether vessels constructed to-day were made of aluminium of greater purity than was the case a few years ago.

Dr. SELIGMAN, referring to the question whether there was a direct comparison between the effect of various acids and these foodstuffs on aluminium, said that there was one very striking case. If lactic acid, equivalent to the amount in milk, were taken, the aluminium would dissolve very readily, but the addition of a little milk to the mixture would stop the attack altogether. That fully illustrated what the President suspected might be the case.

During the last 20 or 30 years there had been an enormous improvement in the quality of aluminium produced, especially in this country. But the point was this: he knew of no aluminium, however inferior, which could have given such results as Dr. Cooper had published.

Mr. SYLVESTER, replying, thanked the President and the audience for the very kind way in which they had received the paper. Referring to the corrosion of aluminium vessels which were not perfectly clean, he mentioned some recent work by Beal (and others) in the April issue of *Industrial and Engineering Chemistry* (ANALYST, 1932, 392). These workers had found a larger amount of aluminium in foodstuffs cooked in stained utensils, thus emphasising the necessity for keeping aluminium vessels scrupulously clean. One speaker had asked whether there would be larger amounts of aluminium present when acid fruits were cooked in aluminium, and Mr. Sylvester quoted figures given in the paper by Beal (and others). Cranberry sauce gave 8 parts per million, which, in the presence of sugar, was decreased to 3. Rhubarb gave 13 parts per million, and in the case of apricots, the aluminium-content increased from 25 to 73. He thought that the latter figure should be accepted with reserve.

The question of cooking in soft water, and the possibility of such water being more corrosive than ordinary tap water had been mentioned, but Mr. Sylvester stressed the fact that the few experiments which had been included in the paper, must not be considered as a scientific investigation of the corrosion of aluminium. They were carried out with the essential object of proving that the method of analysis described was applicable to such problems as corrosion or contamination, and they indicated also the amounts of aluminium likely to occur in foodstuffs as the result of ordinary culinary practice.

Dr. BURN, replying to the question about the action of aluminium on bacteria, said that some work had been done on the subject.

In explanation of the way he had presented the paper he did not pretend that what he said was an impartial survey of the situation. He had already written an impartial survey in the form of a more lengthy report, but it seemed to him that if he were to deal with the subject in twenty minutes the best thing was to put before them the strongest evidence in support of the conviction he had reached.

A New Method for the Determination of Lead in Organic Material, with Special Reference to Dyestuffs

BY NOEL L. ALLPORT, A.I.C., AND G. H. SKRIMSHIRE

(*Read at the Meeting, February* 3, 1932)

THE determination of lead in complex organic material, such as dyestuffs and biological specimens, has always been a troublesome analytical procedure. Gravimetric methods are not well suited to the accurate determination of traces of lead, and even when sufficient material is available to yield weighable quantities of precipitate, the process of separation becomes very complicated when silica or metals such as calcium, iron, or tin are present. It is, therefore, proposed to consider, in this paper, only those processes depending upon colorimetry.

Most of the colorimetric methods depend upon the final conversion of the lead into sulphide, the solution containing the lead being first rendered alkaline. It is obvious that when lead is detected under these conditions, iron and interfering metals must either be absent or, if present, the formation of their sulphides must be prevented. Removal of iron by precipitation as hydroxide is inapplicable, since lead will be adsorbed by the precipitate. In order to eliminate the influence of iron, F. L. Teed (ANALYST, 1892, **17**, 142) proposed the addition of potassium cyanide with the object of forming either ferrocyanides or ferricyanides. This method was elaborated by C. A. Hill (*Chem. and Drug.*, 1905, **77**, 388), who adapted it to the determination of lead in pharmacopoeial chemicals. The processes described are well suited to the purpose for which they were devised, but it is clearly indicated that the presence of iron in more than minute traces will interfere with the colorimetric determination. J. M. Wilkie (*J. Soc. Chem. Ind.*, 1909, **28**, 636) stated that potassium cyanide would eliminate the influence of ferrous iron, but that the ferric iron vitiated the test; he, therefore, recommended preliminary reduction by heating with sodium sulphite or sodium thiosulphate in slightly acid solution, followed by the addition of potassium cyanide and ammonia. In practice, this method frequently proves difficult to operate, and, in any case, it is not

applicable in the presence of more than a few milligrams of iron. Furthermore, with many dyes, even when these are free from iron, the accurate determination of lead by direct methods is not practicable, since the residues remaining after wet oxidation are frequently yellow in colour, owing, probably, to the formation of nitro bodies resistant to further attack by the mixture of nitric and sulphuric acids.

Recently the problem of determining small amounts of lead in biological material has been dealt with by A. G. Francis, C. O. Harvey and J. L. Buchan (ANALYST, 1929, **54**, 725). Briefly, their process involves preliminary wet oxidation of the organic material; the addition of a small quantity of a copper salt; co-precipitation of the lead and added copper by means of hydrogen sulphide; conversion of the sulphides into sulphates, followed by solution in dilute nitric acid, and then separation of the lead from other metals yielding dark coloured sulphides by electrolysis, the lead being deposited as dioxide on the anode. The lead dioxide is dissolved in dilute nitric acid and alcohol, and the lead is precipitated as lead sulphate; this is dissolved in ammonium acetate solution, and the amount of lead present is determined colorimetrically as sulphide. The presence of appreciable amounts of iron will interfere with the electrolytic deposition of lead dioxide, and, in this event, it is necessary to make a preliminary separation of the lead by precipitation as sulphate. The whole process is stated to require about three days to complete, and is, therefore, unsuited for rapid routine work in connection with the examination of dyes and foodstuffs.

Other colorimetric methods for the determination of lead have not proved very satisfactory. The use of tetramethyldiaminodiphenylmethane, suggested by A. Trillat (*Ann. Chim. anal.*, 1903, **8**, 408), involves the electrolytic deposition of the lead as dioxide; in addition to this disadvantage, the reagent yields colours with manganese dioxide and many other oxidising agents.

A process due to L. T. Fairhall (*J. Biol. Chem.*, 1924, **60**, 485) for the determination of lead in urine comprises co-precipitation of the lead with calcium phosphate by rendering the sample alkaline with ammonia, dissolving the lead from the ignited precipitate with dilute nitric acid, conversion of the lead successively into sulphide, sulphate, sulphide and chromate; the chromate is then determined colorimetrically by the use of diphenylcarbazide. In this process the colour produced is due to chromium and not directly to lead. Francis, Harvey and Buchan (*loc. cit.*) criticise this procedure, and also express some doubt as to the efficacy of co-precipitation of lead with calcium phosphate. Again, the process is tedious, since one determination takes six days to complete.

For the diagnosis of plumbism, T. Cooksey and S. G. Walton (ANALYST, 1929, **54**, 97) determine traces of lead in the urine by electrolysing in acid solution, dissolving the lead from the cathode with nitric acid, and removing the latter by evaporation. The residue is then dissolved in hydrochloric acid, and the lead is determined nephelometrically as sulphite. This process, which requires 24 hours to complete, can only be used in those cases where it is known that all the lead is present in an ionisable form.

It occurred to us that diphenylthiocarbazone might prove useful in dealing with the problem under review. The constitution of this compound is represented

by the formula $C_6H_5.N=N.CS.NH.NH.C_6H_5$, and its behaviour towards metals has recently been described by H. Fischer (*Z. angew. Chem.*, 1929, **42**, 1025, and *Mikrochem.*, 1930, **8**, 319), who used a solution in carbon tetrachloride containing a few milligrams of the reagent per 100 c.c. of solvent. This solution is deep green in colour and, when it is agitated with an aqueous alkaline liquid containing lead, the green colour changes to red, owing to the formation of a metallic compound, which is soluble in the organic layer but insoluble in water. Fischer describes the colours produced by several metals under these conditions, and states that the reaction with all metals, lead only excepted, is inhibited by the presence of alkali cyanide. In addition to this, the reagent does not appear to react with iron under any circumstances; it therefore seemed to promise a ready means for the specific removal of lead from the residues remaining after the wet oxidation of organic material. Diphenylthiocarbazone was first prepared by E. Fischer and E. Besthorn (*Annalen*, 1881, **212**, 316) from phenylhydrazine and carbon disulphide. Since it is now an article of commerce, and the pure substance is readily available, further description of its preparation is unnecessary.

DEVELOPMENT OF THE PROCESS.—As this work was undertaken with the object of determining traces of lead in dyestuffs, all the experiments have been conducted on that class of organic material. Since the determination of the lead involves the preliminary destruction of the organic matter by the well-known process of wet oxidation with sulphuric acid and nitric acid, it is obvious that the conditions will be identical for all dyes and all organic substances, subject to such limitations as may be imposed by the presence of various inorganic constituents, apart from the lead. At the outset attempts were made to match the actual red colour due to the presence of lead when the residues from the wet oxidation of lead-containing dyes were diluted with water, then rendered alkaline and mixed with a little potassium cyanide, and finally shaken with very dilute solutions of diphenylthiocarbazone in carbon tetrachloride. It soon proved, however, that this procedure was impracticable, since the gradations of colour produced by varying amounts of lead were too slight to allow of accurate measurement. It was evident that in order to determine the amount of lead extracted it would be necessary to convert the metal into some compound other than the salt of diphenylthiocarbazone. Experiments were, therefore, made, in which the organic solvent containing the lead complex was evaporated, and the dry residue which remained was destroyed by wet oxidation, using only about 0·5 c.c. of sulphuric acid. The resulting colourless acid liquid was then diluted with water, ammonium acetate, excess of ammonia and potassium cyanide were added, and the lead was determined colorimetrically as sulphide in the usual manner.

Working on these lines, promising results were soon obtained, but carbon tetrachloride was found to be unsuitable as a solvent for the reagent, owing to the sparing solubility of diphenylthiocarbazone. A mixed solvent, consisting of three parts by volume of carbon tetrachloride and two parts by volume of benzene, was tried and gave good results, but chloroform was found to be much superior. The reagent ultimately adopted consists of a 0·1 per cent. w/v solution of diphenylthiocarbazone in chloroform. This solution may be stored in stoppered bottles without undergoing deterioration for about a fortnight.

METHOD.—The process, as finally worked out, is as follows:—A suitable quantity of the dyestuff, or other organic material, is destroyed by wet oxidation by heating with sulphuric and nitric acids, and the residue is freed from nitric acid by diluting with water and evaporating until white fumes are evolved. After being cooled, the acid solution is diluted with water, 2 grms. of citric acid are dissolved in the liquid, which is then rendered alkaline with ammonia, and 1 c.c. of 10 per cent. solution of potassium cyanide is added. The cooled solution, which should conveniently amount to 100 to 150 c.c., is transferred to a separator and extracted three times by shaking vigorously with a 0·1 per cent. w/v solution of diphenylthiocarbazone in chloroform. Ten c.c. of the reagent solution should be used for the first extraction, and 5 c.c. each for the second and third. Should the third extraction be bright red in colour, it will be necessary to continue the extraction with more reagent until the red colour is no longer produced. Each extract is washed in turn with about 10 c.c. of water contained in another separator, and transferred to a flask, and the chloroform is evaporated. About 0·5 c.c. of sulphuric acid is added to the residue, and the organic matter is destroyed by heating and adding to the hot sulphuric acid solution a few drops of nitric acid. This residue, which will contain all the lead originally present in the material taken for the determination, is diluted with water, 2 grms. of ammonium acetate are added, and the liquid is rendered alkaline with ammonia. The lead is then determined by adding 1 c.c. of 10 per cent. potassium cyanide solution, then 0·1 c.c. of 10 per cent. sodium sulphide solution, and matching the colour in the ordinary way by means of the Dilute Solution of Lead PbT. of the British Pharmacopoeia (which contains 0·00001 grm. of lead per c.c.), using an auxiliary solution containing 2 grms. of ammonium acetate. If more than 0·1 mgrm. of lead is present, aliquot portions of the solution should be taken, more ammonium acetate being added as necessary.

When examining dyestuffs, it is recommended that the wet oxidation be conducted according to the methods detailed in the First Report of the Sub-Committee on the Determination of Arsenic, Lead and Other Poisonous Metals in Food Colouring Materials to the Standing Committee on the Uniformity of Analytical Methods (ANALYST, 1930, **55**, 102). This report is concerned with the determination of arsenic in colouring materials; hence, provided the relative quantities of the acids used are maintained, it should be admissible to employ a larger amount of the sample at the outset, and to divide the final acid liquid in two portions, one being used for the arsenic determination and the other for the determination of lead.

When a milligram or more of lead is present in the final sulphuric acid residue the lead sulphate will be clearly visible, particularly if all the nitric acid is removed by evaporating down a second time after diluting with water.

The citric acid used in this method serves the two-fold purpose of dissolving lead sulphate present in the sulphuric acid residue, and also of preventing iron from being precipitated when the liquid is rendered ammoniacal. Potassium cyanide is added to the aqueous liquid, prior to shaking with the reagent solution, in order to prevent other metals being extracted by the diphenylthiocarbazone. It is not used to prevent the extraction of iron, since that metal does not react with the reagent

at all; it is, nevertheless, necessary to maintain the iron in solution by the addition of citric acid in order to prevent loss of lead by adsorption. When the amount of lead present is more than a fraction of a milligram the green reagent solution used in the first extraction will turn bright red, and additional portions of reagent will change similarly until all the lead is removed from the aqueous layer. In this way a rough indication of the amount of lead present in the sample is obtained at an early stage of the process. In the absence of lead a considerable proportion of the reagent dissolves in the alkaline aqueous layer, colouring that solution orange. While the reagent itself is soluble in alkaline aqueous media, and is thereby partly extracted from the chloroform solution, the lead compound is insoluble in the aqueous liquid, but readily soluble in chloroform.

TEST EXPERIMENTS.—To test the efficacy of this process, experiments were first made with a specimen of very pure indigo-carmine, practically free from iron. The lead in the sulphuric acid residue from the wet oxidation was determined directly by ordinary colorimetric methods and found to be 30 parts per million. Exactly the same result was obtained when another portion of the same dye was examined by the new process described.

Experiments were made with this same sample of dye to which known amounts of lead had been added, and the results obtained are shown in Table I.

TABLE I

Amount of dye used for the test Grms.	Lead solution added c.c.	Lead solution found c.c.
1	5·0	5·0
2	5·0	4·5
2	20·0	19·0
2	140·0	142·0
5	80·0	80·0
2	500·0	503·5

The quantities of lead in the tables are expressed in terms of the Dilute Solution of Lead PbT. of the British Pharmacopoeia. In quoting the quantity of lead recovered (column 3), the amount of lead originally present in the material, together with the "blank" due to the reagents, has been deducted.

THE INFLUENCE OF OTHER SUBSTANCES.—In studying the effect of other substances on the process, attention was mostly directed to metals, and particularly to iron. Early experiments had shown that the presence of even 1 per cent. of iron in a dye did not interfere with the detection and determination of the lead. A series of tests was now made, in which the proportion of iron in the dye was increased by mixing it with known quantities of ferrous ammonium sulphate, and adding definite volumes of standard lead nitrate solution; the mixture was then submitted to wet oxidation, and the lead was extracted and determined by the process described. In all these experiments a very pure dye was employed, and the lead-content was determined by a colour test applied directly to the residue remaining after wet oxidation. In this way the value of the "blank," due to the

minute trace of lead present in the reagents and the dye itself, was determined independently of the new process. Some of the results of these trials are shown in Table II.

TABLE II

Material treated	Lead solution added c.c.	Lead solution found c.c.	Remarks
1 grm. of dye+0·21 grm. of ferrous ammonium sulphate (=3 per cent. Fe in dye).	10·0	9·5	
2 grms. dye+0·84 grm. of ferrous ammonium sulphate (= 6 per cent. Fe in dye).	7·0	7·6	
1 grm. of ferrous ammonium sulphate	6·0	5·7	
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	10·0	10·0	Used 10 grms. of citric acid. No trace of iron in final matching solution.
5 grms. of ferrous sulphate cryst.	30·0	30·0	Oxidised the ferrous iron by boiling with HCl and $KClO_3$.
2 grms. of ferric sulphate + 1 grm. of ammonium nitrate.	8·0	5·2	Effect of nitrate.
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	500·0	473·0	Used 10 grms. of citric acid.
5 grms. of ferric sulphate [77 per cent. $Fe_2(SO_4)_3$].	120·0	120·0	Used 10 grms. of citric acid.

Another point to which we have given particular consideration is the actual weight of impurity present in the material under examination, as distinguished from the percentage present in the dye. Working on these lines, we found that lead could be added to 5 grms. of ferric sulphate, and be fully recovered and determined colorimetrically. In no case did iron pass through into the final solution, although the added lead was regularly recovered within the limits of experimental error. It was at this stage of the investigation that the mixed solvent of carbon tetrachloride and benzene used to dissolve the diphenylthiocarbazone was abandoned in favour of chloroform, since it was found impossible completely to extract the lead from 5 grms. of iron salt until this modification was tried. On reference to Table II, it will be noticed that ferrous sulphate was oxidised by means of potassium chlorate and hydrochloric acid. When the oxidation was conducted with nitric acid in the presence of sulphuric acid there was difficulty in removing the excess of nitric acid, owing to the tendency towards violent bumping, with consequent loss of material. This residual nitrate tends to interfere with the complete extraction of lead, particularly in the presence of a large proportion of iron. The effect of adding ammonium nitrate to ferric sulphate is shown in the table. Thus, it was proved that iron, even when present in quantity, does not interfere with the determination of lead by this method.

Bismuth.—The process is inapplicable in the presence of bismuth. This metal, if present, will pass through and yield a coloured sulphide. Bismuth is not a likely impurity in dyestuffs, but if this process is applied to toxicological investigations or to metallurgical analysis, special care will, of course, be needed.

Zinc.—Having regard to the fact that some dyestuffs consist of zinc double salts, it was considered important to study the influence of this metal. Reference to Table III shows that the addition of 1·8 grm. of zinc sulphate to a dye does not interfere in any way with the determination of lead. It was observed, however, that when the lead was extracted in the presence of zinc the reagent became bright red in colour, even after all lead had been removed, owing to the reaction with the zinc. Thus, it should be borne in mind that in the presence of much zinc a bright red colour produced by the reagent is not necessarily an indication of a large content of lead.

Aluminium.—Aluminium may cause trouble by reason of the formation of an insoluble anhydrous sulphate during the wet oxidation of the organic material. Reference to Table III will show that where complete solution of the aluminium salt was not effected prior to the extraction process, much of the added lead remained behind as a result of being adsorbed upon the solid suspension. When this experiment was repeated, and the diluted acid liquid was heated for some time with a little potassium sulphate, the soluble alum was re-formed, and complete recovery of the added lead obtained, in the subsequent extraction. Further, to prove this point, an experiment was made with alum itself, and the added lead was satisfactorily recovered.

Copper.—The presence of copper is quite immaterial, provided care be taken to add sufficient potassium cyanide to form the non-ionised complex. While investigating the influence of this metal it was thought that it might be possible to avoid the initial wet oxidation of dyestuffs, and use instead a dry process employing copper nitrate. In order to test this, 2 grms. of the pure specimen of indigo-carmine, previously mentioned as being used for checking purposes, and containing 30 parts per million of lead, were mixed in a porcelain crucible with 3 grms. of anhydrous sodium carbonate and 10 grms. of copper nitrate, $Cu(NO_3)_2.3H_2O$. By the application of gentle heat, using a small Bunsen flame, all organic matter was readily destroyed, and the copper nitrate was decomposed to oxide at a temperature so low that loss of lead by volatilisation could not occur. The cooled residue was dissolved by heating with 20 c.c. of concentrated hydrochloric acid, and the clear liquid, after dilution with water, was treated with citric acid and excess of ammonia, the blue colour of the solution being discharged by the addition of 14 grms. of potassium cyanide. The extraction and colorimetric determination of the lead were then effected by the method already described. The final solution used in the colorimetric determination of the lead yielded a perfect match. A blank experiment on the reagents was made, 2 grms. of lead-free citric acid being used in place of the dye. By this method the lead-content of the dye was found to be 40 parts per million. This procedure is only suggested as a possible alternative to wet oxidation, should the latter be inconvenient to apply. Where the lead-content of the material under examination is low, oxidation with copper nitrate is not recommended, since the value of the "blank" tests is necessarily large; but for organic material containing appreciable quantities of lead the method may well be useful. Experiments have shown that at least 5 mgrms. of lead can be easily and completely extracted from the residue of a copper nitrate fusion.

Tin.—Traces of tin will not influence the working of the process, but if appreciable quantities are present, certain modifications must be introduced. The insoluble "meta-stannic acid" resulting from the wet oxidation should be dissolved. This can generally be accomplished if the sulphuric acid residue is carefully diluted with about 50 c.c. of a 5 per cent. aqueous solution of tartaric acid, and then rendered alkaline with sodium hydroxide solution, care being taken that the temperature does not rise appreciably until the mixture is alkaline. It should then be heated until a clear liquid is obtained. After the addition of a little potassium cyanide the lead is extracted in the ordinary manner. Traces of tin may still pass through with the lead; this trouble can be overcome by evaporating the chloroform and submitting the residue to wet oxidation in the usual way and, after removal of all nitric acid, treating the sulphuric acid residue a second time in the manner just described, and then re-extracting the lead. This somewhat tedious procedure may not always be necessary, and is only indicated in the presence of considerable quantities of tin. Some results obtained in the presence of tin are quoted in Table III.

Calcium phosphate does not interfere. Any material originating from calcium phosphate, or other salts of calcium, contained in the acid residue after wet oxidation should be dissolved by diluting with water and treating with excess ammonium citrate solution. The ordinary process may then be applied.

Silica.—In order to test the effect of appreciable amounts of silica, samples of dye were mixed with dried sodium silicate and, after the addition of known volumes of standard lead solution, they were submitted to wet oxidation. The resulting residues were extracted in the usual way, the insoluble silica being ignored. Full recovery of lead was obtained, thus demonstrating that it is unnecessary to apply any special treatment for the removal of silica.

Nickel.—The process may be applied in the presence of nickel, but it is necessary to guard against incomplete extraction of the lead. Satisfactory results were obtained in the presence of 1 grm. of nickel sulphate when six portions of reagent were used to remove the lead from the aqueous solution.

Cobalt also tends to retard the removal of lead, notwithstanding the presence of an excess of potassium cyanide. This difficulty was surmounted by heating the solution containing cobalt with sufficient ammonium chloride, ammonia and hydrogen peroxide to produce a cobaltammine. After excess hydrogen peroxide had been boiled off, a little hydrazine sulphate was dissolved in the solution to reduce any lead peroxide which might have been formed. Citric acid and 1 c.c. of 10 per cent. solution of potassium cyanide were then added, and the usual procedure was followed.

Silver, mercury, manganese, and *chromium* do not interfere with the extraction and determination of lead. An exhaustive examination of the influence of these four metals has not been made, but the experiments quoted in Table III would suggest that none of them is likely to cause much difficulty.

From a consideration of the work here described it would appear that diphenylthiocarbazone might be applied to metallurgical analysis. Our process has been designed for the purpose of dealing with traces of lead, but it may be

TABLE III

Material treated	Lead solution added c.c.	Lead solution found c.c.	Remarks
1 grm. dye + 0·022 grm. of zinc sulphate (= 0·5 per cent. Zn in dye).	5·0	5·0	
2 grms. dye + 0·88 grm. of zinc sulphate (= 10 per cent. Zn in dye).	20·0	20·0	
2 grms. dye + 1·8 grm. of zinc sulphate (= 20 per cent. Zn in dye).	95·0	98·0	Used 1 grm. of potassium cyanide.
2 grms. dye + 0·175 grm. of potassium alum (= 0·5 per cent. Al in dye).	8·0	8·0	Aqueous liquid before extraction of lead was clear.
2 grms. dye + 3·5 grms. of potassium alum (= 10 per cent. Al in dye).	5·0	2·2	Aqueous liquid before extraction of lead was hazy. Lead adsorbed.
2 grms. dye + 3·5 grms. of potassium alum (= 10 per cent. Al in dye).	10·0	10·0	Aqueous liquid cleared by heating after addition of potassium sulphate.
5 grms. potassium alum	10·0	9·8	
1 grm. dye + 0·4 grm. of copper sulphate (= 10 per cent. Cu in dye).	8·0	8·2	Used 2 grms. of potassium cyanide.
1 grm. dye + 0·0095 grm. stannous chloride (= 0·5 per cent. Sn in dye).	6·0	5·8	Used tartaric acid and sodium hydroxide.
5 grms. dye + 0·0475 grm. of stannous chloride (= 0·5 per cent. Sn in dye).	25·0	26·4	Lead extracted once only. Sulphide colours did not match well.
2 grms. dye + 0·38 grm. of stannous chloride (= 10 per cent. Sn in dye).	4·0	3·6	Extracted the lead a second time. Perfect colour match obtained.
2 grms. dye + 1 grm. of calcium phosphate.	10·0	9·5	Added excess ammonium citrate solution to residue after wet oxidation.
2 grms. dye + 2 grms. of calcium phosphate.	6·0	6·5	Added excess ammonium citrate solution to residue after wet oxidation.
2 grms. dye + 0·5 grm. of dried sodium silicate.	10·0	10·0	Aqueous liquid before extraction of lead contd. insoluble silica in suspension.
2 grms. dye + 2·0 grms. of dried sodium silicate.	15·0	15·0	Aqueous liquid before extraction of lead contd. insoluble silica in suspension.
2 grms. dye + 1·0 grm. of nickel sulphate (= 10·4 per cent. Ni in dye).	10·0	10·2	Used 2 grms. of potassium cyanide and six portions of reagent solution.
2 grms. dye + 1·0 grm. cobalt nitrate (= 10 per cent. Co in dye).	10·0	10·0	Heated with NH_4Cl + NH_4OH + H_2O_2. Reduced PbO_2 with $N_2H_4.H_2SO_4$.
2 grms. dye + 0·5 grm. of silver nitrate (= 15·9 per cent. Ag in dye).	5·0	5·0	Used 2 grms. potassium cyanide.
2 grms. dye + 0·5 grm. of mercuric chloride (= 18·5 per cent. Hg in dye).	5·0	5·2	Used 2 grms. potassium cyanide.
2 grms. dye + 2 grms. of manganous sulphate + 1 grm. potassium permanganate.	10·0	10·0	Added HCl to residue after wet oxidation.
2 grms. dye + 0·5 grm. of potassium dichromate.	8·0	7·8	

possible by making suitable modifications, such as increasing the strength of the reagent solution, to extract much larger quantities of lead from its association with other metals.

SUMMARY.—A new method has been described for the determination of lead present in organic material. The whole process can easily be completed in two hours, and is, therefore, eminently suited to the routine examination of dyestuffs required for medicinal and food-colouring purposes.

A special feature of the process is its applicability in the presence of large quantities of iron. It has been shown that traces of lead present in salts of iron can be detected and accurately determined.

Bismuth interferes with the test, and special procedures are necessary when appreciable amounts of tin, aluminium, nickel or cobalt are present.

Silica and calcium phosphate do not present any difficulties, and large quantities of copper, zinc, silver, mercury, manganese, and chromium may be present without vitiating the determination of the lead.

In conclusion, we wish to record our thanks to Mr. T. T. Cocking, F.I.C., for his valuable advice and interest during the course of this work, and to the Directors of The British Drug Houses, Ltd., for permission to publish the results of the investigation.

Investigations on Milk Standards under the Burma Food and Drugs Act, 1928

BY EDWIN H. BUNCE, F.I.C.

(*Read at the Meeting, February* 3, 1932)

A LARGE number of samples of both cow's and buffalo's milk, from herds and from individual animals, were examined throughout a period of eleven months.

The herds were systematically studied at regular intervals, so that seasonal variations could be observed and a fair average obtained.

In the case of the individual animals, however, the samples were taken at random from various localities, the object being to study the quality of milk of the poorest types of animals. The animals were chosen on the advice of an officer from the laboratory, specially deputed for the purpose, and he also witnessed the milkings.

The yield of morning milk was greater than that of evening milk drawn from the same animals, but the milk was of poorer quality in respect of fat. These results, of course, are associated with the interval between the milkings. In general, the period from evening to morning was 13 to 14 hours, and that from morning to evening 10 to 11 hours. Exceptionally, in the case of the buffalo herds during the months of August to November, the period from evening to morning was 15 to 16 hours, and that from morning to evening 8 to 9 hours. This was, perhaps, unfortunate, but unavoidable, and consideration of the results obtained demonstrates still more forcibly the effect of milking at unequal intervals.

Cow's Milk.—The number of mixed herd samples examined was 200. The fat and total solids were determined directly by the usual analytical methods, and in a few instances these figures disagreed with Richmond's formula.

The average results of all samples were:

Table I

	No. of samples	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.	Ash Per Cent.	Sp.gr.	Acidity*
Morning milk	100	3·63	9·30	12·93	0·76	1·0333	1·5
Evening milk	100	5·19	9·30	14·49	0·74	1·0325	1·5
Average	All samples	4·41	9·30	13·71	0·75	1·0329	1·5

* Number of c.c. of $N/10$ sodium hydroxide solution per 10 c.c. of milk.

The average figure for solids-not-fat was remarkably constant, and no appreciable variation was observed in the average figure for fat throughout the period of the investigation. These facts are brought out clearly in Table II. No herd samples gave a percentage of solids-not-fat below 8·5 per cent., and only one gave a fat figure below 3·0 per cent.

The number of samples examined from individual cows was 90. As already mentioned, these samples were taken from different localities, and were in no way connected with each other. In some cases the animals could hardly be said to be properly kept and fed. Such milk is sometimes exposed for sale, however, and that was the main reason for their inclusion in the investigation.

In two cases the solids-not-fat were below 8·5 per cent., and seventeen samples gave a fat figure below 3·0 per cent.

Standards.—No legal standards for cow's milk are at present in operation in Burma, but the laboratory has adopted a minimum of 3·0 per cent. for fat, and 8·5 per cent. for solids-not-fat. The latter figure is a lenient one, and although a number of samples gave slightly less than 3·0 per cent. of fat, only one of these was from the mixed herd. Since the greater part of milk for sale is the product of more than one animal, the standard of 3·0 per cent. for fat cannot be said to be stringent.

Table II

Average Percentage of Fat and Solids-not-fat in Mixed Samples from Herds

	Period	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.
Morning milk	April–July	3·74	9·28	13·02
Evening milk	April–July	5·09	9·30	14·39
Average	April–July	4·42	9·29	13·71
Morning milk	August–November	3·49	9·21	12·70
Evening milk	August–November	5·29	9·21	14·50
Average	August–November	4·39	9·21	13·60
Morning milk	December–March	3·71	9·40	13·11
Evening milk	December–March	5·14	9·40	14·54
Average	December–March	4·42	9·40	13·82
All samples	April–March	4·41	9·30	13·71

TABLE III

SHOWING SAMPLES GROUPED ACCORDING TO THEIR FAT AND SOLIDS-NOT-FAT CONTENT

Total No. of samples	Below 3·0 per cent. fat		3·0–3·5 per cent. fat		Below 8·5 per cent. solids-not-fat		8·5–9·0 per cent. solids-not-fat	
	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.
200 (from herds)	1	0·5	38	19·0	—	—	20	10·0
90 (from individuals)	17	18·9	10	11·1	2	2·2	31	34·4

BUFFALO'S MILK.—The number of mixed herd samples (from *Bubalus buffalus*) examined was 200. The analytical methods employed were precisely the same as those adopted for cow's milk.

The average results of all samples were:

TABLE IV

	No. of samples	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.	Ash Per Cent.	Sp.gr.	Acidity*
Morning milk	100	6·78	10·16	16·94	0·79	1·0336	1·2
Evening milk	100	7·98	9·92	17·90	0·77	1·0330	1·0
Average	All samples	7·38	10·04	17·42	0·78	1·0333	1·1

* Number of c.c. of $N/10$ sodium hydroxide solution per 10 c.c. of milk.

Again it will be seen from Table V, below, that the average figure for solids-not-fat is remarkably constant. The drop in fat-content for the morning milk, with a corresponding rise for the evening milk, during the period August to November, is accounted for by the change in the times of milking, as given above. However, it will be noticed that the results obtained by averaging the fat-content of both morning and evening milk during this period, in no way deviate from the other average figures similarly obtained. No herd samples gave a percentage of solids-not-fat below 9·0, and only three samples gave a fat figure below 5·0 per cent.

The number of samples examined from individual buffaloes was 76. These samples were taken at random, and the same statements apply as in the case of individual cow samples in this respect.

In no case was the figure obtained for solids-not-fat below 9·0 per cent., although there were several only just above that figure. The fat-content of two samples was below 5·0 per cent.

Standards.—As in the case of cow's milk, standards for buffalo's milk have not yet been legally defined in Burma. A minimum of 5·0 per cent. for fat, and of 9·0 per cent. for solids-not-fat, is applied in the laboratory in passing judgment on samples. No final opinion on the purity or otherwise of a sample of milk received for analysis is given, however, without recourse to cryoscopic examination.

Similar remarks apply to samples of cow's milk submitted for analysis.

TABLE V

AVERAGE PERCENTAGE OF FAT AND SOLIDS-NOT-FAT IN MIXED SAMPLES FROM HERDS

	Period	Fat Per Cent.	Solids-not-fat Per Cent.	Total solids Per Cent.
Morning milk	April to July	7·16	9·96	17·12
Evening milk		7·90	10·00	17·90
Average		7·53	9·98	17·51
Morning milk	August to November	5·94	10·29	16·23
Evening milk		8·58	9·99	18·57
Average		7·26	10·14	17·40
Morning milk	December to March	7·06	10·11	17·17
Evening milk		7·64	9·88	17·52
Average		7·35	10·00	17·35
All samples	April to March	7·38	10·04	17·42

TABLE VI

SHOWING SAMPLES GROUPED ACCORDING TO THEIR FAT AND SOLIDS-NOT-FAT CONTENT

	Below 5·0 per cent. of fat		5·0–5·5 per cent. of fat		Below 9·0 per cent. of solids-not-fat		9·0–9·5 per cent. of solids-not-fat	
Total No. of samples	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.	No. of samples	Per Cent.
200 (from herds)	3	1·5	9	4·5	—	—	1	0·5
76 (from individuals)	2	2·6	4	5·3	—	—	18	23·7

APPLICATION OF CRYOSCOPY

Rigid control of the milk supply is a much more complicated problem in India and Burma than in England, mainly owing to the fact that the milk of at least two animals of different species is involved.

The milk from cows and buffaloes is often mixed indiscriminately, with or without the addition of water or other substances, but more often the buffalo milk is watered so as to mimic the composition of cow's milk, and then sold as such. Buffalo's milk being much richer in every respect, the fraud has been perpetrated with great success, water being added in almost every proportion.

It was obvious from this that the ordinary standards alone were hopelessly inadequate, and that some other means would have to be evolved to check adulteration effectively. The cryoscopic method suggested itself as a possible solution of the problem, since it was noticed that the soluble salts of the two milks approached more closely to each other than any of the other constituents normally present.

An apparatus modelled on the principle of the Beckmann cryoscope was employed, the accessories being readily available. The more elaborate Hortvet type would have been preferred, but, owing to the difficulty experienced in procuring that apparatus in reasonable time, its adoption would have meant the

curtailment of cryoscopic measurements during the first six months of the investigation.

Application of correction factors was avoided by a carefully standardised procedure, so that the results obtained were strictly comparable. As a preliminary experiment the accuracy of the method was demonstrated with a series of known mixtures of authentic samples with water.*

All the samples described above were tested. They were perfectly fresh in all cases, and showed no tendency to souring.

A summary of the results is given in Tables VII and VIII.

TABLE VII

COW

Total No. of samples	Range	Average
200 (from herds)	−0·550° C. to −0·580° C.	−0·573° C.
90 (from individuals)	−0·550° C. to −0·580° C.	−0·567° C.

TABLE VIII

BUFFALO

Total No. of samples	Range	Average
200 (from herds)	−0·560° C. to −0·590° C.	−0·579° C.
76 (from individuals)	−0·560° C. to −0·590° C.	−0·578° C.

In view of these results a freezing-point figure outside the ranges shown must be considered unsatisfactory, and for the purpose of deducing the percentage of added water −0·550° C. has been adopted as the freezing-point of cow's milk, and −0·560° C. as that of buffalo's milk.

The relatively small difference of 0·01° C. between the two values is of greatest importance. Such difference corresponds with less than 2 per cent. of added water. Any attempt, therefore, to water buffalo's milk so that the lower standards for cow's milk are complied with is almost impossible, and cannot fail to escape detection if a cryoscopic examination is carried out.

My thanks are due to my Chief Assistant, Mr. G. C. Moitra, B.Sc., who carried out a considerable amount of the experimental work, and also to the other members of my staff who materially assisted in the investigation.

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* The apparatus was filled with a mixture of crushed ice and salt to serve as a freezing medium. A sufficient quantity of the sample (previously cooled) to submerge completely the thermometer bulb was placed in the freezing-tube, and the thermometer, together with the stirrer, was inserted. The test tube was then lowered into the larger tube of the apparatus.

Uniform stirring at the rate of about once per second was then applied, and the temperature of the cooling bath was adjusted, so that a supercooling of the sample between 1·0° and 1·5° C. was readily obtained. The mercury column rose rapidly to its highest point, when the reading was taken after tapping the upper end of the thermometer two or three times. By this method ten to twelve determinations were easily carried out within an hour.

The zero point of the thermometer was ascertained by observing the freezing-point of recently boiled and cooled distilled water under the same conditions. This point was checked whenever a new series of determinations was made.

Care was taken that the curvature of the bottom of the freezing-tube was not too pronounced; otherwise efficient stirring was difficult.

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.

MILK OF THE AMERICAN BUFFALO

Two samples of buffalo (*Bison americanus*) milk, submitted by the Veterinary Research Station, Lethbridge, Alberta, have recently been analysed in these laboratories. The first sample, received February 1st, and to which 0·1 per cent. of formalin had been added as a preservative, had slightly curdled in transit. The second sample, received March 19th, and to which 0·25 per cent. of formalin had been added, was perfectly sweet and fluid on arrival at Ottawa. Analysis gave the following results:

	No. 1	No. 2
Specific gravity	—	1042·0
Total solids (direct determination) ..	12·97 per cent.	13·67 per cent.
Fat	1·83 ,,	1·69 ,,
Casein	3·66 ,,	4·24 ,,
Albumin	0·64 ,,	0·54 ,,
Lactose	3·73(?) ,,	5·74 ,,
Ash	0·86 ,,	0·96 ,,

Owing to the partial coagulation of the milk, some of the results obtained with the Sample No. 1 are doubtful, so that the analysis cannot be accepted as absolutely representing the composition of the fresh milk.

The following pertinent information respecting the buffalo producing the milk has been kindly furnished by Mr. L. M. Heath, the officer in charge of the Station.

"Born May, 1924. Received at the Veterinary Research Station from Wainright Buffalo Park, December 4th, 1924.

"Kept in corrals from date of receipt until October, 1926; then turned into pasture with other domestic cattle.

"Bred to domestic polled bull (no particular breed), July–August, 1928. Calved June, 1929 (first hybrid offspring).

"Bred to domestic polled bull, January 8th, 1931. Calved November 1st, 1931 (second hybrid offspring).

"The milk samples you analysed were collected as follows:—The first (curdled) sample, January 26th, 1932; the second, March 15th, 1932.

"It will be seen, therefore, that the samples were collected on the eighty-seventh and one hundred and thirty-sixth days, respectively, after the second gestation period.

"No great difficulty was experienced in collecting the samples of milk. Restraint was, of course, necessary, and was procured by means of a 'squeeze.' The 'squeeze' in question is a narrow alleyway, one side of which is adjustable, so that pressure can be brought to bear on an animal in the alleyway to prevent undue movement, the animal being in the natural standing position. The samples were obtained by hand-milking.

"There is no great mammary development in the buffalo as compared with that of cattle, and its teats are rather short. Owing to the small size of the udder the milk secretion is of necessity limited in quantity, and it was estimated that not much in excess of a litre was secreted overnight (about 15 hours) at the time the second sample was collected for your analysis."

FRANK T. SHUTT.
(*Dominion Chemist.*)

DEPARTMENT OF AGRICULTURE,
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MECHANICAL WOOD PULP IN PAPER

THE determination of the mechanical wood content of papers by the phloroglucinol method, which forms the subject of a recent communication by Dr. Dunnicliff and Mr. Suri (ANALYST, 1932, 354), has of late become of greater importance, in consequence of the Indian Import Tariff on papers, "in which the mechanical wood pulp amounts to not less than 65 per cent. of the fibre content," and it has been stated that raising the percentage to 70 per cent. is being considered.

It has been all too apparent, however, that the use of the phloroglucinol method, unstandardised to Indian conditions, is unreliable. The method used by Cross and Bevan, which has been widely used, was not standardised, and had certainly not been devised with any regard to its present-day importance. Messrs. Dunnicliff and Suri have now standardised the process systematically.

The other available method most widely used is the "fibre count" microscope method of examining a series of mounts and estimating, by eye, the relative proportions of the fibrous ingredients present; the average accuracy for a series is no better than *plus* or *minus* 5 per cent. for ordinary fibres, and probably no better than *plus* or *minus* 10 per cent. for mechanical wood, which is always present in lumps and clumps. This method was formerly used in India in assessing tariff duty payable and, not unnaturally, its use gave rise to difference of opinion and dissatisfaction. In dealing with borderline and disputed cases, the method of Cross and Bevan was used to confirm or reject the report based on the optical method. For the reasons given in paragraph 2 (v.s.), the assessment by this method was also sometimes disputed.

In 1929 Dr. Dunnicliff undertook the detailed examination of the phloroglucinol method and standardised the conditions of test. I understand from him that the old "fibre count" method has been discarded, that a Spence and Krauss weight-length method is now officially authorised at the Custom House Laboratories in India, and that complaints are now comparatively rare.

In disputed cases the phloroglucinol method, as set forth by Dunnicliff and Suri (*loc. cit.*), is used at the Control Laboratory of the Central Board of Revenue. They recommend a standard temperature of 35° C., and they define standard conditions which will enable reproducible determinations to be made, accurate to about *plus* or *minus* 1 per cent. This is clearly a great advance on methods hitherto available, and it is satisfactory to know that it has become the official method for confirming tariff duty payable in India.

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Notes from the Reports of Public Analysts

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

COUNTY PALATINE OF LANCASTER

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1931

THE total number of samples examined during the year was 5448, of which 5146 (3010 formal and 2136 informal) were foods and drugs; of these, 139 were returned as adulterated.

MILK.—One hundred and twelve (3·7 per cent.) of the 3010 samples examined were adulterated.

"APPEAL-TO-COW" SAMPLES.—The earliest reference to "appeal-to-cow" samples appears to be that in the report of the Local Government Board (now the Ministry of Health) for 1879 in connection with Salford. "The Analyst states that if samples taken at the station correspond with former adulterated samples, he makes a point of seeing the cows milked and analyses a sample obtained in his presence, so as to leave no chance of an innocent person being convicted."

It has not been possible to determine exactly when the first sample was taken in the County of Lancaster, but complete records are available since the year 1903. Tables showing the composition of "appeal-to-cow" samples from that year until 1931 are published in this Report.

The Freezing-Point of Milk.—Since this work was started in the County Laboratory 211 samples of genuine milks have been examined. The determined freezing-point depression has varied between 0·530° C. and 0·561° C., with an average figure of 0·543° C. This figure agrees substantially with those found by all other observers whose work has been published, or which is personally known to the writer (*cf.* ANALYST, 1930, **55**, 423).

With regard to abnormal samples, in every case so far investigated the abnormality has taken the form of a greater depression rather than a smaller, so that, although the addition of a little water to an abnormal milk might pass on the evidence of the freezing-point alone (even this possibility is much reduced by the taking of "appeal-to-cow" samples), it is most unlikely, in fact, almost impossible, that a genuine milk would be suspected of being watered.

Mathieu and Ferré's Formula.—This denotes the sum of the weight of crystallised lactose and of the sodium chloride expressed as the (isotonic) equivalent of lactose. The value of this constant for most milks is said to be between 74 and 79, and to be reduced below 74 when any considerable quantities of extraneous water are present (*J.S.C.I.*, 1914, **33**, 214).

This method has been examined by various workers (Mathieu, *J.S.C.I.*, 1916, **35**, 613; Ferris, *J.S.C.I.*, 1917, **36**, 1245; Sirot and Joret, *J.S.C.I.*, 1919, **38**, 475A; Fonzes-Diacon, *J.S.C.I.*, 1919, **38**, 787A; and Joret and Radet, *B.C.A.*, 1927, 794B), who have found this suggested constant to vary more than had originally been supposed. Figures varying between 69·2 and 82·8 have been reported.

The "Cryolac Number."—P. Post (*B.C.A.*, 1926, 846B) has introduced what he terms the "cryolac number." This is an expression which is obtained by calculating the theoretical freezing-point due to the lactose and chlorides (calculated as common salt), both of which are determined chemically. Fiehe and Kordatzki (*B.C.A.*, 1928, 687B) found that the cryolac number accounted for 75 per cent. of the total freezing-point depression, and that it varied between 393 and 435, with a mean of 413.

The observed variation in the freezing-point, as between one genuine milk and another, is less than that in the case of the cryolac number, so that, in general, the former method is to be recommended. In cases where the freezing-point cannot be determined, however, the cryolac number may be of use, particularly for sour milks, as it takes into account the acidity of the sample.

CREAM CONTAINING GLYCERIN.—An informal sample, containing 4·7 per cent. of glycerin, was returned as adulterated. The addition of glycerin to food is not prohibited by the Preservatives Regulations, but it has been shown that in quantities of the order of 5 per cent. glycerin has little, if any, preservative action; in fact, the sample in question was slightly sour when received. The addition was probably made in a misguided attempt to improve the appearance of the article.

GRAVY BROWNING.—One sample, submitted as a browning for fish, was described on the label as follows: ". . . is new-laid eggs and golden toasted rusks."

It was found to contain not more than 2 per cent. of dried eggs, which must be regarded as unsatisfactory, in view of the statement on the label, and, more particularly in view of the colour of the sample, which might be thought to give support to the claims made.

Another sample contained 0·13 per cent. of ferric oxide, which might have been added as a colouring agent.

HEALTH SALTS (LIME JUICE AND SULPHUR SALTS).—A sample, described on the label as "Lime Juice and Sulphur Salts," was found to consist of a mixture of sugar, tartaric acid and sodium bicarbonate, with a small amount of sulphur. There was also present a small amount of essential oil of lime, but this was the only ingredient present that could be said to have any connection with lime juice. In view of the very considerable therapeutic value which is assigned to lime fruit, the description of this sample must be considered as unsatisfactory. The mixture did not even contain citric acid.

LEMONADE POWDER.—A sample, described as "lemonade powder," consisted of a mixture of cane sugar and tartaric acid, flavoured with oil of lemon; there was no citric acid.

ORANGE SQUASH ESSENCE.—A sample, which was described as "Orange Squash Essence" and was labelled "Pure Orange Squash to make 20 glasses of Orange Squash," consisted of a 20 per cent. solution of citric acid, which was flavoured with the pulp and essential oil of orange. The composition of this sample, compared with those of two samples, sold respectively as "concentrated orange juice" and as "orange squash," was as follows:

	Total solids Per Cent.	Citric acid Per Cent.	Proportion of citric acid to total solids Per Cent.
Orange squash essence ..	23·4	22·7	97·1
Concentrated orange juice ..	67·2	6·3	9·4
Orange squash	41·6*	2·1	5·1

* Contained added cane sugar.

From these figures and the general character of the sample, it is obvious that this article was, for the most part, an artificial mixture intended to counterfeit the natural article.

JAM.—The percentage of total soluble solids in the 65 jams examined has varied between 67·1 and 75·4 per cent., with the exception of one sample, which was as low as 63·7 per cent., as determined by the refractometer. In all cases the amount of insoluble solids has also been determined, and the results obtained, together with others obtained during the year 1930, are given in the following table:

INSOLUBLE SOLIDS IN JAM, PER CENT., 1930–31

	Number	Average	Highest	Lowest
Blackcurrant	19	2·17	2·98	1·29
Strawberry	44	1·19	2·28	0·52
Raspberry	23	2·14	3·00	0·72
Apricot	6	1·04	2·76	0·44
Damson*	13	0·81	1·73	0·40
Red plum	2	—	0·51	0·48

* Without stones.

ZINC IN CANNED LOBSTER.—A sample of canned lobster contained zinc to the extent of two-thirds of a grain per pound, calculated as metallic zinc. There was no indication that the zinc had been derived from the container. Traces of copper

are not infrequently present in lobster, but so large an amount of zinc as this is unusual.

TURMERIC IN PEPPER.—One sample of pepper was found to contain a small amount of turmeric. None of the other 801 samples examined during the last six years has contained more than a trace of turmeric.

ACETIC ACID AS "PURE VINEGAR."—A sample of diluted acetic acid, coloured with caramel, was labelled as "An unfermented vinegar for household use." It might very well be argued that this is a contradiction in terms, the word "vinegar" —originally applied to sour wine, which is now described as wine-vinegar—being usually given to a fermented product. For some time now diluted acetic acid has been described by some persons as "Pure Vinegar"; they have even gone so far as to claim that such a "Pure Vinegar" is better, as it does not include the "Impurities" usually present in ordinary vinegar. An analogous proposition would be the description of diluted alcohol as "Pure Wine," and it is to be feared that the introduction of the term is merely an attempt to pass off an inferior article on the reputation of a better.

G. D. ELSDON.

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.

LIABILITY OF MANUFACTURER FOR INJURIOUS DEFECTS IN HIS PRODUCTS

M'ALISTER OR DONOGHUE (PAUPER) *v.* STEVENSON

IN this case the House of Lords, by a majority of three to two (Lord Atkin, Lord Thankerton and Lord Macmillan; Lord Buckmaster and Lord Tomlin dissenting), allowed the appeal from a judgment of the Second Division of the Court of Session in Scotland, which, by a majority of three to one, had reversed the decision of the Lord Ordinary (Lord Moncrieff). Judgment was given on May 26th, 1932.

The appellant, a shop assistant, claimed £500 damages from the respondent (a manufacturer of aerated waters), for the injurious effects alleged to have been caused by the presence of a dead snail in a bottle of ginger beer manufactured by the respondent. The bottle was of dark opaque glass, so that its contents could not be ascertained by inspection, and was closed with a metal cap.

It was agreed by counsel on each side that the English and Scots laws on the subject were identical.

Lord Atkin, in delivering judgment, said that the question was whether, as a matter of law, the respondent owed any duty to the appellant to take care. He pointed out that in English law there must be, and was, some general conception of relations giving rise to a duty of care, of which the particular cases found in the books were but instances. But acts or omissions which any moral code would censure could not, in a practical world, give a right to every person injured by them to demand relief. Rules of law had arisen which limited the range of complaints and the extent of their remedy. Reasonable care must be taken to avoid acts or omissions which one could reasonably foresee would be likely to injure one's neighbour. In law one's neighbour seemed to be persons who were so closely and

directly affected by one's act that one ought reasonably to have them in contemplation when directing one's mind to the acts or omissions which were called in question. That appeared to him to be the doctrine in *Heaven* v. *Pender* (11 Q.B.D., 503, 509), as laid down by Lord Esher, when it was limited by the notion of proximity, introduced by Lord Esher himself, and by Lord Justice A. L. Smith in *Le Lievre* v. *Gould* (1893, 1 Q.B., 491).

With that necessary qualification of proximate relationship, he thought that the judgment in *Heaven* v. *Pender* expressed the law of England. No doubt cases would arise where it would be difficult to determine whether the contemplated relationship was so close that the duty arose. But he could not conceive any difficulty in the class of case before the Court. A manufacturer put up an article of food in a container, which he knew would be opened by the actual consumer. There could be no inspection by any purchaser, and no reasonable preliminary inspection by the consumer. Negligently, in the course of preparation, he allowed the contents to be mixed with poison. It was said that the law of England and Scotland was that the poisoned consumer had no remedy against the negligent manufacturer. If that were the result of the authorities, he would consider the result a grave defect in the law. Not only would the consumer have no remedy against the manufacturer, but he would have none against anyone else for negligence; and, except in the case of a consumer, who was also a purchaser, there would be no contract and no warranty of fitness; and if a specific article were purchased under its patent or trade name, there would be no warranty protecting the purchaser-consumer. There were other articles, such as many forms of goods sold for cleaning purposes, to which the doctrine supported by the decision below would apply. The manufacturer knew that the articles would be used by persons other than the actual ultimate purchaser—namely, by members of his family, his servants, and, in some cases, his guests. He did not think so ill of their jurisprudence as to suppose that its principles were so remote from the ordinary needs of civilised society and the ordinary claims it made on its members, as to deny a legal remedy where there was so obviously a social wrong.

In his opinion, several of the authorities supported the view that, in such a case as the present, the manufacturer owed a duty to the consumer to take reasonable care in the preparation or putting up of the products, when the absence of such reasonable care was likely to result in injury to the consumer's life or property. It was a proposition which, he ventured to say, no one in Scotland or England, who was not a lawyer, would for one moment doubt. It would be an advantage to make it clear that the law in this matter, as in most others, was in accordance with sound common sense. He thought that the appeal should be allowed.

Lord Thankerton and Lord Macmillan agreed that the appeal should be allowed.

SALE OF A POISONOUS DISINFECTANT BY GROCERS

Council of the Pharmaceutical Society of Great Britain *v.* Brown

On May 9th, a Divisional Court of the King's Bench Division dismissed the appeal of the Council of the Pharmaceutical Society against a judgment given by Judge Higgins at Brentford County Court in favour of the defendant (Analyst, 1932, 30).

The proceedings were instituted under Sec. 15 of the Pharmacy Act, 1868, which provides that any person not being a duly registered pharmaceutical chemist, or chemist and druggist, who sells a poison to which the Acts apply, shall be liable to a penalty not exceeding £5; and under Sec. 12 of the Pharmacy Act, 1852, which provides that all penalties under the Acts may be recovered as a civil debt in the County Court.

An inspector in the employment of the appellants had bought from the respondent, a grocer, a bottle of Izal in a bottle described as the "Universal Pack," and analysts were called at the County Court trial to prove that the article contained more than 3 per cent. of homologues of carbolic acid. The County Court Judge held that if, as in this instance, the preparation was sold with a notice that it was intended for use in agriculture or horticulture, the section had been complied with.

Mr. Justice Acton, delivering judgment, said that the crucial question was whether the preparation came within the exception contained in the latter part of the definition in the Schedule. The qualification covered by the words exclusively, distinctively and definitely could not be introduced. It was sufficient for the defendant to show that the article had been prepared for some purpose in connection with agriculture and horticulture. He need not show that it was exclusively so prepared, or that it could not be used for any other purpose. It was argued for the appellants that the label on the bottle was a pretence which did not in any sense represent the true purpose for which the article was made up and sold. But there was ample evidence that the preparation had been sold for many years for agricultural and horticultural purposes, the only difference being that, until recently, it had been packed in tins instead of bottles. He considered, therefore, that the appeal should be dismissed.

Mr. Justice Talbot gave judgment to the same effect.

EGG BAKING POWDER

Alleged False Label

On May 31st, at Saltash Police Station, a manufacturing firm was summoned, under Sec. 30 of the Sale of Food and Drugs Act, 1928, for having sold an article—Egg Baking Powder—which was falsely described on the label. Mr. C. Knight, who prosecuted on behalf of the Cornwall County Council, said that the major point of the prosecution was that there was no egg in the sample, and that the label was therefore fraudulent; secondly, if there were 1 per cent. of egg in the sample, which was not agreed by the prosecution, the label was still fraudulent, and the submission of the prosecution was that 1 per cent. would not be sufficient to justify the label. The County Council had a duty to the retailer and a duty to the public in that it had to see that they were not misled into buying that for which they had not asked. The certificate of the Public Analyst, Dr. H. E. Cox, said that the sample was coloured baking powder of satisfactory composition, but, as it did not contain any egg, was not correctly described as Egg Baking Powder.

Dr. Cox, giving evidence, said that the powder contained 67 per cent. of cereal and about 33 per cent. of a mixture containing bicarbonate of soda, tartaric acid, acid sodium pyrophosphate, and a trace of dye. He found 3·5 per cent. of proteins, 0·58 per cent. of fat, and 0·02 per cent. of organic phosphoric acid; he was of opinion that these were all attributable to the cereals, and he found no definite evidence of egg. He agreed that there might be 0·1 or 0·2 per cent., but regarded 1 per cent., which was suggested by the Government Chemist, as an over-estimate, as the amounts of protein, fat and organic phosphorus were, within experimental error, the same as those he found in baking powder of the same manufacture not alleged to contain egg. An experiment was shown demonstrating that 1 per cent. of egg in such a mixture could be separated by flotation, whereas none could be so separated from this sample. If the powder did, in fact, contain 1 per cent. of dried egg, a cake made in accordance with the directions on the label would contain only about 1/10,000th part of egg. In his opinion, a powder labelled "Egg Baking Powder" ought to contain quite a substantial proportion of egg.

Mr. Wolferstan, defending, referred to the case heard before the Saltash Bench last August (Analyst, **1931**, **56**, 661), and said that the manufacturers had recalled

and re-labelled the product "Egg Baking Powder," and considered that they had done everything to keep within the four corners of the Act.

A certificate from the Government Chemist was produced, which stated that the sample consisted of baking powder coloured yellow, containing a small proportion of dried egg, which had been identified microscopically, and expressed the opinion that it contained about 1 per cent. of dried egg.

Mr. T. Tickle, County Analyst for Devon, said that he had analysed the sample and found commercial dried egg yolk amounting to 0·75 per cent.; he had since seen the manufacturers' formula, which showed 1 per cent. of dried egg yolk. He would not expect nutritive value in baking powder, and, if the powder were called egg baking powder, he would not expect nutritive value in it.

The manager of the defendant's firm stated that the recipe included a definite quantity of dried yolk of egg, and that he superintended the manufacture.

After a retirement the Bench announced that they must convict, fined the defendants £5, and ordered them to pay 5 guineas costs.

The National Physical Laboratory

REPORT FOR THE YEAR 1931*

THE Report for 1931 follows the same general arrangement as that for 1930 (ANALYST, 1931, **56**, 661). A general survey of the work is made in the Report of the Executive Committee; a comparison of tests for 1929, 1930 and 1931 follows, and a list of published papers for 1932, official and unofficial, occupies some 11 pages. The Reports of the Superintendents of the different departments deals with details of the work, and a few investigations only can be mentioned here. A detailed description of the new Physics building is given.

GOVERNMENT RESEARCH.—Among the special investigations, the study of the crystalline structure of teeth was continued, in conjunction with the Dental Disease Committee of the Medical Research Council; the constituents of both enamel and dentine have been found to be identical with that of apatite, but the crystals are arranged at random in the dentine, and with a marked selective orientation in the enamel, so that the [001] directions of the crystals are inclined at an angle of approximately 20 to the normal to the surface of the tooth in human teeth, but the [001] of canine teeth coincides with the normal to the surface. *X*-ray photographs showed that the dentine contains much more amorphous material than the enamel.

STANDARDS OF MEASUREMENT.—Work towards the establishment of international standards of candle-power for work at higher colour temperatures than that corresponding with the colour of the primary unit, has involved measurement by the national laboratories of France, Germany, United States, and Great Britain, of the transmission of 4 blue glasses supplied by the Reichsanstalt, Berlin, which, used with a carbon-filament lamp of colour temperature 2,080° K, give light of colour temperature 2400° K, that is, approximately the colour temperature of a tungsten-filament vacuum lamp. A discussion of the measurements resulted in agreement that the spectrophotometric method of measurement gave the most concordant results, and that this method would be accepted and standards adjusted accordingly.

RELATIVE PERMEABILITY OF VARIOUS MATERIALS TO WATER VAPOUR.—Waxed paper was found to be of low permeability, compared with treated (soaked

* Department of Scientific and Industrial Research. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 15s. net.

in medicinal paraffin) and untreated brown paper; calico treated with mutton fat had a permeability of one-third that of treated brown paper. Parchment paper is about 4 times as permeable as treated brown paper, so that, commencing with the lowest, the order of permeability is: White waxed paper, calico impregnated with mutton-fat, brown paper soaked in paraffin, and parchment paper.

EFFECT OF TEMPERATURE ON THE RELATIVE "SPREADABILITY" OF BUTTER.—Extrusion under measured pressure through a sharp-edged orifice was adopted as a means for comparative tests. Butters of different origin and blends of butter were tested over a range of temperatures. Other points investigated were (*a*) the effect of "working" the sample, (*b*) the effect of prolonged storage at temperatures well below freezing-point, and (*c*) the effect of storage at temperatures near the freezing-point.

OPTICS.—*Colour Measurement and Standardisation.*—The agreement reached at the meeting of the International Commission on Illumination on the subject of colorimetry accepts the principle developed at the Laboratory (ANALYST, **1931, 56,** 662), with certain changes in detail. The "basic stimulus"* of the system finally selected is an "equal energy spectrum," and the primaries—necessarily hypothetical stimuli—are so chosen that all colorimetric quantities are expressible by positive numbers. The "luminosity factors" of the primaries are respectively 0 : 1 : 0. The distortion of the colorimetric scales, *i.e.* the variation in the significance of given small changes in the colorimetric co-ordinates in different parts of the field, is as small as possible. To the three homogeneous radiations adopted as the primaries of the laboratory system, and to a heterogeneous stimulus from a specified lamp and filter combination of very similar colour and energy distribution to the N.P.L. standard white are ascribed definite co-ordinates, and the list of spectral coefficients defining the proposed standard observer has been transformed from the laboratory to the new system and adopted as the international standard. The laboratory instruments have been re-calibrated in terms of the new system, but no alteration is involved in the experimental procedure to be followed by practical colorimetrists, but only a reduction of results, and an explanatory paper is being prepared to facilitate the use of the system.

METROLOGY.—*Volumetric Glassware and Hydrometers.*—The drafting of standard specifications for glassware and for the testing of milk and milk products has been undertaken by the glassware sub-committee of the Dairy Research Committee of the Empire Marketing Board, and a very extensive series of experiments has been necessitated. The work on the surface-tension of milk has resulted in the average value at ordinary room temperature being taken as 45 degrees per cm., and variations are unlikely to exceed 5 degrees per cm. Proposals for a standard lactometer are being prepared in which, when the above figure for the surface tension is used as a basis for the standard, errors due to variation of the tension should not exceed 1 in 10,000. Standardisation of standard specific gravity hydrometers has been carried out in conjunction with surface-tension measurements over a range of specific gravity from 0·9000 to 1·300.

METALLURGY.—*Study of Special Alloy Systems.*—Much attention has been given to methods of melting aluminium alloys, and of removing dissolved gases, including bubbling of nitrogen through the metal (which is often effective), introduction of a volatile chloride, *e.g.* titanium chloride or carbon tetrachloride, and a combination of the two methods. Final conclusions have not yet been reached.

* This term has recently been suggested by I. G. Priest, of the Bureau of Standards, to denote the stimulus which is colorimetrically matched by numerically equal "quantities" of the primaries of a trichromatic system. In the system hitherto employed in the Laboratory the "primaries" are homogenous radiations of wave-lengths 0·700μ (red), 0·5461μ (green), and 0·04358μ (blue), and the "basic stimulus" is the radiation given by the particular lamp and filter combination hitherto known as the National Physical Laboratory standard white light.

Work on the age-hardening and rolling properties of some magnesium alloys has necessitated the use of a flux to protect the metal against the action of the air, and crucibles of austenitic chromium-nickel steel had to be used. The study of magnesium-manganese alloys has been begun; so far, the maximum of manganese possible to introduce into the alloy is 5 per cent. An alloy of magnesium containing 0·15 per cent. of beryllium has been prepared.

Study and Improvement of Methods of Metallurgical Analysis.—The testing of high-chromium, high-nickel rust-resisting steels used in the second heightening of the Aswan Dam has shown some slight modifications in methods to be desirable. The effects of impurities in copper have involved intricate analyses, and the observations of Hampe on the constitution of minute residues of antimonates of bismuth remaining insoluble after the solution in nitric acid of copper containing antimony, bismuth and oxygen, have been confirmed. To facilitate the analysis of alloy steels, an apparatus for determining sulphur has been installed.

British Standardised Steel Samples.—Accurately standardised steels by means of which analytical methods can be tested have been prepared, in collaboration with District Authorities representative of the local university or equivalent institution, and of the works or commercial laboratories of the district. No samples are sent out until final values have been accepted after substantial agreement between all the analysts and a definite limit of possible error can be stated. The standards available, each analysed for one element (impurity) only, are:

No. 1. .. Sulphur (S=0·027 per cent.).
No. 2. .. Sulphur (S=0·071 per cent.).
No. 3. .. Phosphorus (P=0·029 per cent.).
No. 5. .. Carbon (C=0·65 per cent.). Acid O.H. steel.
No. 6. .. Carbon (C=0·10 per cent.). Basic O.H. steel.
No. 8. .. Carbon (C=0·27 per cent.). Acid O.H. steel.
No. 9. .. Carbon (C=1·09 per cent.). Acid O.H. steel.
No. 11. .. Manganese (Mn=0·69 per cent.). Acid O.H. steel.
No. 12. .. Cast iron standard sample (Si=2·22 per cent., P=1·14 per cent., Mn=0·50 per cent., S=0·075 per cent.).

D. G. H.

Ministry of Agriculture and Fisheries

AGRICULTURAL PRODUCE (GRADING AND MARKING) ACT, 1928

STATUTORY RULES AND ORDERS, 1930, No. 370

Agricultural Produce (Grading and Marking), England, Order No. 370 (ANALYST, 1931, **56**, 108) has been superseded by S.R.O., No. 458, of 1931 (Fruits), and No. 442, of 1931 (Vegetables). These orders are obtainable from H.M. Stationery Office, price 1d. each. No. 458 is in terms similar to No. 370, but includes, in addition to the fruits therein named:

Select raspberries and redcurrants
Select dessert cherries
Select Morello cherries
Select cultivated blackberries
Select redcurrants

The strength of syrup in which they are to be packed remains the same, *viz.* 40 per cent. for plums and 45 per cent. for the others.

Order No. 442 (Vegetables) defines the quality of select beans (whole and sliced), beetroots, carrots (whole), celery (hearts), peas, new potatoes, spinach, turnips (whole), macedoine of select vegetables; it also gives a list of the varieties of plums, apples, cherries and peas which shall be used, and an experimental schedule of minimum fruit weights and net weights.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Non-Homogeneity of Casein. Fractionation by means of Ammonium Chloride. E. Cherbuliez and M. L. Schneider. (*Helv. Chim. Acta*, 1932, **15**, 597–609.)—By fractional precipitation of a solution of casein in dilute sodium hydroxide or ammonia solution by means of ammonium chloride, it is shown that casein consists of two components, termed α- and β-caseins, which are respectively insoluble and soluble in the ammonium chloride solution. The proportion of the β-form, which is highly hygroscopic, is between five and eight times that of the α-form. The percentage compositions of the two fractions and of the original casein are as follows:

	C	H	N	S	P
Casein ..	52·45	7·21	15·59	0·64	0·84
α-Casein ..	52·52	7·12	15·25	0·61	0·72
β-Casein ..	52·60	6·88	15·34	0·75	2·32

That the separation is not accompanied by hydrolysis of the casein is shown by the facts that the neutralisation equivalents of the α- and β-forms differ little from that of casein, and that the proportion of formol nitrogen is higher in casein than in either α- or β-casein. The optical rotation of a 1 per cent. solution in 0·01 *N* NaOH is $[\alpha]_D = -111°$ for each of the three compounds.

α-Casein resembles casein in properties, whereas the β-form shows appreciably different behaviour, its solubility relations, for instance, approaching more nearly those of the globulins than those of casein. β-Casein (1 part) dissolves rapidly in aqueous pyridine (200 parts) at the ordinary temperature, whereas α-casein is almost insoluble in this solvent. From its 3 per cent. solution, α-casein, like casein itself, is coagulated by rennet to give a dense curd, whilst the β-modification yields only a slight coagulum without markedly altering the fluidity of the liquid.

T. H. P.

Prediction of the Extract of Malt by Bishop's Barley Formula. W. J. Mitchell. (*J. Inst. Brewing*, 1932, **38**, 241–244.)—Bishop (*J. Inst. Brewing*, 1930, **36**, 421) has shown that, for Plumage–Archer barleys of one strain, the extracts of the malts obtained therefrom can be predicted from the equation, $E = 110·1 - 11·2\,N + 0·18\,G$, where E is the extract in brewers' lbs. per quarter of dry malt, N is the percentage of nitrogen in the dry barley, and G is the weight in grms. of 1000 corns of the dry barley. This equation is applicable to barleys which have been grown under widely varying conditions (soil, weather, manuring). Moreover, by suitable modification, the equation may be rendered valid for barleys of another variety; *e.g.* for Spratt–Archer barley, $E = 110·6 - 11·2\,N + 0·18\,G$.

The author has collected the nitrogen-contents and 1000-corn weights of 279 samples of kiln-dried barley, mostly of second grade and representative of the production of most of the barley-growing districts of Scotland and Northumberland for a single season, together with the mean values calculated by taking into account

the weights of the different lots. These mean values are, for the dry barley: nitrogen, 1·62 per cent., and 1000-corn weight, 40·73 grms. During the corresponding malting season, the brewers' extract was determined for each of 126 samples of malt made from barleys of the same origin. Application of Bishop's Plumage–Archer formula to the mean figures for the barleys gives, for the predicted extract of the resulting malt, 99·3 lbs. per quarter, whereas the actual mean value for the malts examined is 98·9 lbs. It is, therefore, suggested that subtraction of 0·4 (*i.e.* 99·3–98·9) from the right-hand side of this equation will yield a formula allowing of the prediction of the extracts of malts made from Scotch barley of second grade.

Further confirmation of the usefulness of Bishop's formula is obtained from the results furnished during a period of six years by 20 samples of high-grade Scotch barleys of known history. Each of these barleys, which differed widely in regard to conditions of growth, was malted in a 20-quarter experimental malting. The average figure found for the predicted extract of the malt was 99·7 lbs., and the average actual extract of the malt, determined by the standard laboratory method, was 99·8 lbs. per qr. With only three of the samples is the agreement between actual and calculated extract unsatisfactory. In two of these three cases, the malting losses were abnormally high, so that Bishop's formula becomes invalid, but the third case is not explainable in this way. The formula may also be used when a method other than the standard method is employed for determining the amount of extract yielded by the malt, provided that the "equation constant" (110·1) is suitably changed. T. H. P.

Colorimetric Estimation of the *p*H Value of Wort or Beer. P. Kolbach. (*Wochenschr. f. Brauerei*, 1932, **49**, 81–85.)—The results obtained when the *p*H of wort or beer is measured by the ordinary comparator method are subject to errors due to the following causes: (1) The colour of the indicator (especially if two-colour) may be not quite the same in wort or beer as in a buffer solution of similar *p*H value. (2) The indicator may be adsorbed to some extent by the colloids of the wort or beer, and its colour may be affected by oxidising or reducing substances present. (3) The salts in the buffer solution used in the colour comparison have an influence on the colour not exerted by the wort. The first two of these sources of error are avoidable by eliminating the cells containing water and untreated wort, respectively, a mixture of the sample, indicator and buffer solution being matched against a mixture of sample, indicator, and water in similar proportions. The indicator is then in a similar medium in each of the two mixtures, except for the salts of the buffer solution; this "salt error" may be reduced by using 0·1 *N* sodium chloride solution, instead of water, in the other mixture.

The procedure to be followed is described in detail. The indicators recommended are: bromocresol green (*p*H 4·0 to 4·8), methyl red (4·8 to 5·6) and bromocresol purple (5·6 to 6·4), and use is made of a series of succinate buffers covering the total range of *p*H values with steps of 0·2. The salt corrections, which are given for the three indicators and for worts of various specific gravities and various degrees of attenuation, usually amount to only 0·05 or 0·1. The results obtained by this method are correct to within 0·1. T. H. P.

"Ketone Rancidity" of Fats. I. New Method of Detection. K. Täufel and H. Thaler. (*Chem. Ztg.*, 1932, **56**, 265–266.)—The following reaction, based on the formation of red condensation products of salicylaldehyde with higher aliphatic ketones, is capable of detecting the ketone rancidity of fatty products, such as butter and margarine, in its early stages:—From a 200-c.c. distilling flask, provided with a ground-in stopper and delivery tube, and charged with 180 c.c. of water and a few scraps of material to prevent bumping, 25 to 30 c.c. are distilled through a short Liebig condenser into a large test-tube. Pure salicylaldehyde (0·4 c.c.) is added to the distillate, which is vigorously shaken to give an emulsion. After the aldehyde has settled, all but about 4 c.c. of the water is poured away, the contents of the tube being then emulsified again. Two c.c. of pure sulphuric acid are then poured in a stream (not down the side of the tube) into the liquid, which is afterwards well shaken. When the tube is left at rest for a short time, the salicylaldehyde separates, leaving a lower milky layer. This blank experiment should give an aldehyde layer with no more than a very faint pink (usually a faint yellow) colour. Into the water (about 150 c.c.) remaining in the distilling flask, 10 grms. of the fat to be examined are introduced by means of a long funnel. The subsequent procedure is that followed in the blank experiment. If the fat contains even traces of ketone, the layer of salicylaldehyde separating from the sulphuric acid shows a distinct pink colour. As the intensity of the coloration usually increases if the liquid is heated for a short time, it is advisable, especially when only a weak colour reaction is given, to place the tubes from both the blank and the actual experiment for 15 minutes in a boiling water-bath.

The colour given, under the above conditions, is orange with acetone, and deepens as the carbon-atom chain of the ketone lengthens, so that methyl-nonyl-ketone gives an intense raspberry-red colour. The reaction is not given by aldehydes or by those aromatic ketones which have been examined. A distinct coloration is obtained with coconut fat (10 grms.) to which methyl-nonyl-ketone, in the proportion of 1 to 500,000, has been added. The apparatus must be scrupulously cleaned with boiling caustic alkali solution, and then with hot nitric-sulphuric acid mixture before use, and the employment of water prepared by electro-osmosis or of rubber or cork connections must be avoided. If commercial salicylaldehyde is to be used, its preliminary purification by means of the bisulphite compound is necessary. T. H. P.

Philippine Rice Oil. (Ramai variety.) A. O. Cruz, A. P. West and V. B. Aragon. (*Phil. J. Sci.*, 1931, **48**, 5–13.)—Rice bran (polishings) contains oil which readily hydrolyses. Ramai rice is a Philippine lowland variety, with rather large grains; the dry bran contained about 18 per cent. of oil, which, when clarified, was dark brown with a greenish tinge, and had the following characteristics:—Sp.gr., 30°/4° C., 0·9059; n_D^{30}, 1·4662; saponification value, 185·9; iodine value (Hanus), 99·3; acid value, 42·2; unsaponifiable matter, 4·0 per cent.; saturated acids (corrected), 19·9; and unsaturated acids (corrected), 69·7 per cent., with iodine value 124·7. The saturated and unsaturated acids occurring as glycerides were separated, and by application of the lead salt and ether method, by the preparation of the bromine derivatives of the unsaturated

acids, and by esterification of the saturated acids the composition (expressed as glycerides) of the oil was calculated as oleic, 45·3; linolic, 27·6; myristic, 0·1; palmitic, 16·9; stearic, 2·6; arachidic, 0·5; and lignoceric acid, 0·9; and unsaponifiable matter, 4·0 per cent. This is very similar to the composition of kapok and cottonseed oils, and rice oil appears suitable for similar purposes, but, owing to the difficulty of expression, would appear to need extraction plant for its commercial production. D. G. H.

Composition of Philippine Talisay Oil from the Seeds of *Terminalia Catappa*. A. O. Cruz and A. P. West. (*Philippine J. Sci.*, 1932, **48**, 13–19.)—*Terminalia catappa*, L, is a tree reaching 25 metres in height, which grows in the Philippines near the sea shore, and has seeds with edible kernels yielding talisay oil, known in India as Indian almond oil. The whole seeds contained about 3 per cent. of oil, or about 52 per cent. in the kernels, and the oil had specific gravity at 30° C./4° C., 0·9046; $n_D^{30°}$ C., 1·4644; saponification value, 193·2; iodine value (Hanus), 75·4; unsaponifiable matter, 0·54 per cent.; acid value, 2·5; saturated acids (corrected), 32·62; unsaturated acids (corrected), 61·01 per cent., with iodine value 122·9. The saturated and unsaturated acids were separated, and the composition (expressed as glycerides), eventually calculated as oleic, 40·85; linolic, 22·91; myristic, 1·00; palmitic, 28·47; stearic, 3·99; and arachidic acid, 0·75; and unsaponifiable matter, 0·54 per cent. D. G. H.

Rapid Method for the Determination of the Amount of Sodium Nitrite in Pickling- and Preserving-Salt. J. Peltzer. (*Chem. Ztg.*, 1932, **56**, 383.)—The sample (10 grms.) is dissolved in 150 c.c. of water and neutralised, if necessary, to phenolphthalein. It is then boiled with 15 c.c. of 0·1 *N* sulphuric acid and a little pumice until the nitric oxide liberated according to the equation, $3NaNO_2 + H_2SO_4 = Na_2SO_4 + NaNO_3 + 2NO + H_2O$, is removed, and the excess of acid is then titrated with 0·1 *N* alkali (1 c.c. acid ≡ 0·0103515 grm. $NaNO_2$). Qualitative or quantitative tests for the nitrate formed in this reaction may also be applied. Thus, an aliquot portion of the solution is mixed with three times its volume of concentrated sulphuric acid, and the cooled mixture (nitro-sulphonic acid) is shaken with brucine, the red colour being then matched with that given by a standard solution treated in a similar way. J. G.

Identification of Corynanthine. J. Sidvadjian. (*J. Pharm. Chim.*, 1932, **124**, 352, 353.)—The following reactions appear to be similar for yohimbine and its optical isomer, corynanthine. In Fröhde's reaction, both dissolve to give a blue colour; with Mandelin's reagent a violet colour, and with Meillère's reagent, also, (dilute sugar solution and concentrated sulphuric acid) a violet colour is formed. Further, if a few mgrms. of vanillin or of piperonal are added to a solution of either substance, and concentrated sulphuric acid is then poured in, a violet colour is formed. An addition of a few mgrms. of corynanthine, or of yohimbine, and of the same quantity of chloranil to 2 c.c. of epichlorhydrin gives, on boiling, a brown coloration, and the addition of concentrated nitric acid to the cooled liquid changes the colour to cherry-red. D. G. H.

New Reaction of Aconitine and of the Total Alkaloids of Aconite. C. Brugeas. (*Ann. Falsificat.*, 1932, **25**, 147–149.)—Aconitine itself gives a red-violet coloration in Monti's reaction (sulphuric acid and resorcinol heated on a water-bath), but, when made alkaline with strong sodium carbonate solution, the liquid becomes colourless with a blue fluorescence. If, however, the residue extracted from a preparation of aconite (prepared by Ogier's modification of the Stas method) is used, the red-violet colour changes, on rendering the solution alkaline, to an intense purple with green fluorescence. The shade of purple varies with the concentration of the alkaloid, but the fluorescence persists, although gradually fading on standing. A positive reaction is indicative of the presence of the total aconite alkaloids. D. G. H.

Biochemical

Halibut-Liver Oil as a Source of Vitamin *A*. J. A. Lovern. (*Nature*, 1932, **129**, 726.)—The author has confirmed the fact, reported by other workers, that the liver oil of the halibut (*Hippoglossus vulgaris*) is a very rich source of vitamin *A* (of the order of 50 to 100 times as rich as cod-liver oil). All potencies from 30 blue units (0·2 c.c. of 20 per cent. solution) up to 1600 blue units have been observed, but not all samples of halibut-liver oil were found to give such high values, and this irregularity appears to be the rule and not the exception. Therefore, if halibut-liver oil is to become of commercial value as a ready-made vitamin *A* concentrate, as is hoped, it is necessary to know something of these fluctuations, whether they are seasonal, etc., especially as halibut-liver oil cannot be obtained by steaming the livers, but needs the more expensive process of solvent extraction. A series of experiments on this problem of the excessive fluctuations in vitamin *A* potency of halibut-liver oil is being carried out, and attempts will be made to find the seasonal effects (if any), and the influence of the diet of the fish concerned. P. H. P.

Sparing Action of Fat on Vitamin *B*. II. Rôle played by Melting-Point and Degree of Unsaturation of Various Fats. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, 1932, **96**, 165–177.)—It has been previously shown by the authors (*J. Biol. Chem.*, 1929, **83**, 269) that the liberal inclusion of fat in the diet will enable an animal to withstand for many weeks the withdrawal or omission of the antineuritic vitamin *B*, and that in the presence of fat more growth will occur at any definite level of vitamin *B* than with a fat-free diet. The effectiveness of lard and cottonseed oil was reported. It was thought important to determine whether the sparing action of a fat was in any way related to its physical properties, such as melting-point and degree of unsaturation. Samples of cottonseed oil, perilla oil, coconut oil and lard were used, also some synthetic, some hydrogenated, and some partly hydrogenated samples. It was found that, provided a fat melts near body temperature, neither its precise melting-point nor the degree of saturation plays an important rôle in the remarkable ability to spare the amount of vitamin *B* required for any definite growth performance. Fats melting at or above 62° C. are very poorly absorbed by the rat, and do not exhibit the above sparing action. Fats melting at 38° C. have just as effective sparing

action as those which are liquid at room temperature. Fats almost saturated and possessing an iodine value of 8 are as effective as highly unsaturated fats with an iodine value of 187. To judge of the sparing action of any fat it was necessary to determine the degree of absorption. The food consumed was recorded, and the fat-content of the faeces was determined by extracting the faeces with hot benzene, and weighing the dried extract. P. H. P.

Sparing Action of Fat on Vitamin *B*. III. Rôle played by Glycerides of Single Fatty Acids. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, 1932, **96**, 179–188.)—It was felt that a deeper insight could be had into the problem by the use of fats consisting of the glycerides of single fatty acids. Attempts to carry out this project are described. Pure caprylic, capric, lauric, myristic, palmitic, and stearic acids, and their glycerides were prepared and tested on rats. The results show that, in the absence of vitamin *B*, some glycerides of single fatty acids permit better growth than do natural fats such as cottonseed oil. The glycerides differ among themselves, those of myristin and caprylin being more effective than the others. In the presence of vitamin *B*, however, natural fat is superior to any of the single glycerides. The glyceride of stearic acid exerts no sparing action on vitamin *B*; in fact, the animals on this diet are in poorer condition than those on the fat-free diet. The poor growth performance of the animals receiving stearin can perhaps be attributed to the fact that it is very poorly absorbed, its bulk in the food causing a partial starvation. The glycerides of single fatty acids which permit better growth than do natural fats in the absence of vitamin *B*, do not possess properties in common, such as melting-point or length of chain. P. H. P.

Crystalline Vitamin *D*. C. E. Bills and F. G. McDonald. (*J. Biol. Chem.*, 1932, **96**, 189–194.)—In a recent communication, Bills, McDonald, BeMiller, Steel and Nussmeier (*J. Biol. Chem.*, 1931, **93**, 775) noted that the crystalline preparations of vitamin *D* reported by English and German workers had less antirachitic potency than certain non-crystalline preparations of their own. This observation has led to renewed and successful efforts to induce crystallisation in the active resinous products already described. It is shown that the potencies reported for several crystalline preparations of vitamin *D*, when translated into international units, reveal wide variation in antirachitic value. The known tendency of impure sterols to remain vitreous when cooled below their melting points suggested that crystallisation was but a matter of time. Several active resins of the same order of potency as several crystalline preparations, which had been put aside and protected from decomposition, were examined. Slow crystallisation was observed to occur in material which had stood for several weeks. At first only scattered islands of fine needles were seen; these gradually became rosettes, which, under magnification, resembled chestnut burrs. The older preparations were solid crystalline masses. It is significant that an activated ergosterol preparation, known to be impure, changed completely into a crystalline mass merely on standing. Therefore, under suitable conditions, a resinous preparation can pass into the crystalline state without change of purity. The crystalline state is evidence of relative, not absolute, purity in vitamin *D*. The

best crystalline preparations as yet described are probably isomorphous mixtures containing a large percentage of inert material; they should be regarded as starting material for further fractionation. P. H. P.

Unsaturated Fatty Acids in Diet. II. H. M. Evans and S. Lepkovsky. (*J. Biol. Chem.*, 1932, **96**, 157–164.)—In studies on the physiological importance of fats to the animal organism, Evans and Lepkovsky (*J. Biol. Chem.*, 1929, **83**, 269) became convinced that progress could be made only when individual fatty acids were used; only when synthetic fats composed of single fatty acids are used in experimental diets will it be possible to accumulate a body of data which will lead to a better understanding of the rôle played by fats in the animal organism. The investigation now described is concerned with the rôle of single saturated fatty acids when vitamin *B* and, in fact, all the known vitamins, are adequately supplied. When glycerides of single fatty acids were used as the sole source of energy in the diet, certain phenomena akin to those obtained in studies on fat-free diets were shown, with some similarities, but some vital differences. The results show that animals do not thrive on diets which contain the essentials hitherto known (adequate amounts of protein, all of the known vitamins, and the essential inorganic constituents), but in which the energy requirements are met by the glycerides of saturated fatty acids. Glycerides of saturated fatty acids, when given as the sole source of energy, do not promote growth in the rat equal to that obtained with sucrose as the sole source of energy. Unsaturated fatty acid preparations containing fatty acids with more than one double bond markedly improve such diets. Oleic acid produces a very slight response, whereas linolic acid produces a marked response. The natural fats were superior in every case to the synthetic fats.

P. H. P.

Toxicological

Chromium Toxicology. Absorption of Chromium by the Rat. L. W. Conn, H. L. Webster and A. H. Johnson. (*Amer. J. Hyg.*, 1932, **15**, 760–765.)—Owing to the increasing use of "18–8" chromium-nickel steels for dairy machinery, the toxic effect of minute quantities of chromium has been investigated. Rats on chromium-free diet were housed in glass cages, in some cases with chromium-plated copper or chromium-plated nickel floor rods. In other cases rats were fed with milk previously kept for 3 hours at 60 to 65° C. in chromium nickel-steel containers, and, in still further experiments, they were fed with milk containing chromium lactate corresponding with 0·25, 0·5, 1, 10, 50, and 100 parts of chromium per million. The rats were then killed, and the alimentary tract was washed out and, together with the body, was dried and ashed, and the ash analysed. The chromium was determined by dissolving 1 to 5 grms. of ash in hot dilute hydrochloric acid, oxidising any chromium with sodium peroxide and boiling off the excess, diluting the cold solution to 200 c.c., centrifuging to throw down the calcium hydroxide, and determining the chromium in 100 c.c. of the supernatant liquid by Stover's diphenyl-carbazide method. (*J. Amer. Chem. Soc.*, **50**, 2363.) The only positive results were obtained with rats fed on milk containing the three largest amounts of chromium (10, 50 and 100 parts per million), which showed,

respectively, 0·0023, 0·002 and 0·002 mgrm., which meant that only 0·03, 0·006, and 0·003 per cent., respectively, of the chromium given was retained. Since these small amounts were found in rats which had been given milk containing 20 to 200 times as much chromium as the largest amount found in milk kept in chromium-nickel-steel utensils, the menace to the public health from the use of such utensils is regarded as negligible. The presence of chromium in the food to the extent of 100 parts per million was found to have no ill effect on the general health or reproductive powers of the rats, and, further, it is not retained, but promptly and completely eliminated by the rat. In one case only of those in which the rats were in cages with chromium-plated floor-rods was any chromium found in the ash. D. G. H.

Bacteriological

Action of Penicillium on Artificial Silks. T. F. Heyes and H. S. Holden. (*J. Text. Inst.*, 1932, **23**, T79.)—It is already known that when a mixture of cotton and artificial silk becomes mildewed it is only the cotton which is attacked. Five types of artificial silk (acetate, nitrocellulose, viscose, stretch-spun and parallel-spun cuprammonium) were tested for resistance to five species of Penicillium:—*P. purpurogenum* var. *rubri sclerotium*, *P. pinophilum*, *P. lilacinum*, and two strains isolated from mildewed American cotton yarn and from black-stained mercerised cotton. About 1 grm. of each silk was wound round a glass reel, about 3 inches long, and sterilised in a plugged glass tube for 20 minutes in the presence of sufficient culture medium just to touch the silk. With each silk five series of cultures were made, the following liquids being used for wetting out:—Water, 1 per cent. asparagine solution, 1 per cent. ammonium nitrate solution, 1 per cent. potassium nitrate solution, 1 per cent. peptone solution. After inoculation with the Penicillium, growth was allowed to proceed for 3 months, after which, the cultures were removed, the silks were tested for breaking load, the fractured ends were examined microscopically, and the copper number was determined. The most resistant type of silk was the sample of acetate silk. Considerable tendering of a silk may take place through mould-growth, without the damage being visible microscopically. Stretching in the spinning process appears to confer some power of resistance on non-esterified silks. The same type of damage on any one sample was produced by the various species of Penicillium. The effects of asparagine, peptone, etc., vary, and the order of resistance of the silks, other than acetate, does not allow of generalisation. Full results are given in 8 tables. R. F. I.

Organic Analysis

Micro-Analytical Method for the Identification of Organic Substances. V. Stanék and T. Nemes. (*Chem. Ztg.*, 1932, **56**, 285–287.)—The method depends on the experimental determination of the "oxidation-value" of the substance in terms of potassium iodate, and comparison of this result with the theoretical value obtained from the sum of the iodate-oxidation equivalents of the individual atoms suspected to be present. The formula (14·268 × per cent. C + 42·466 × per cent. H + 81·207 × per cent. S − 9·167 × per cent. N − 5·351 ×

per cent. O) gives the theoretical percentage of potassium iodate required, and is deduced from the chemical equations expressing the oxidation of each of the individual elements. In the determination, 100 to 150 mgrms. of pure, powdered potassium iodate are weighed out to within 0·01 mgrm., and dissolved in 2 to 3 c.c. of warm concentrated sulphuric acid in a test-tube. A known weight of sample (1/10 to 1/30 of the amount of iodate taken) is weighed in a small glass dish, or if liquid, in a capillary tube, which is dropped into the test-tube and broken up with a glass rod, and the whole is heated in a sulphuric acid-bath at 190 to 205° C. (I_2O_4 forms at 230° C.). When no more gas is evolved, and the solution is colourless, it is cooled, washed with 50 c.c. of water into 100 c.c. of water in a flask, and the mixture is then boiled in the presence of a little pumice until all the free iodine is removed. The excess of iodate in the colourless solution is then titrated after addition of 1 grm. of potassium iodide, by means of sodium thiosulphate solution, with starch as indicator. The error in oxidation value for substances which are easily attacked (*e.g.* carbohydrates) is about ± 0·5 per cent., but volatile or more resistant substances (*e.g.* naphthalene, picric acid, osazones, halogen and sulphonated derivatives and hydrochlorides) give unreliable results. Ions which interfere with the iodate titration should, of course, be absent. It is suggested that in certain cases the iodine should be removed by distillation and collected and titrated, and it is also often necessary to determine the ammonia formed from any nitrogen present by distillation, and to apply confirmatory tests (*e.g.* m.pt.) to the original substance. J. G.

Method of Determining (Aromatic) Aldehydes, based on Cannizzaro's and Claisen's Reactions. L. Palfray, S. Sabetay and D. Sontag. (*Compt. rend.*, 1932, **194**, 1502–1505.)—The reaction $2R{\cdot}CHO + KOH \rightarrow R{\cdot}CO_2K + R{\cdot}CH_2{\cdot}OH$ does not proceed to completion when aromatic aldehydes are heated with an ethyl or butyl alcohol solution of potassium hydroxide, but it becomes quantitative when the alkali is dissolved in benzyl alcohol (b.pt. over 200° C.). The aldehyde (1 to 2 grms.) and 20 to 25 c.c. of 0·5 *N* solution of potassium hydroxide in benzyl alcohol are kept gently boiling for 2½ hours in a 150-c.c. conical flask of green or Jena glass (acid glass, such as Pyrex and Sibor, should be avoided), fitted with a long air-condenser tube. After addition of water, the liquid is titrated in presence of phenolphthalein to determine the residual excess of alkali. The result is corrected for that obtained in the same manner, but without the aldehyde. Benzaldehyde, anisaldehyde, tolualdehyde, cuminaldehyde and salicylaldehyde may be accurately determined by this method, which is applicable also to natural products containing aromatic aldehydes. T. H. P.

Fats of Brown Sea-weeds. B. Russell-Wells. (*Nature*, 1932, **129**, 654–655.)—In order to determine any relation between depth of immersion and the nature of the fatty constituents, four sea-weeds were examined, representing a range of habitat from a minimum covering by sea-water at spring tides in the case of *Pelvetia canaliculata libera*, to a period of being uncovered only at the same season for *Laminaria digitata*, and including the intermediate *Pelvetia canaliculata* and the slightly deeper growing *Fucus vesiculosus*. The petroleum spirit extract, and also the percentage of true fat, decreased from 8·0 and 6·2 per cent. (on the

dry material) for the least immersed weed, to 0·3 and 0·16 per cent. for the most deeply immersed. The extracts were separated into unsaponifiable residue and fatty acids, and the iodine values of these, as found by the pyridine bromine method, showed no relationship similar to that of the above figures. The unsaponifiable residue, however, calculated as a percentage of the petroleum spirit extract, increased with depth of immersion. The fatty acids from the sea-weeds showing the two extremes of habitat were separated into solid and liquid portions, solid acids for *Pelvetia libera* and *Laminaria digitata* comprising 11·5, 17·7 per cent., and the liquid acids 78·7 and 72·2 per cent. The general character of the fats does not appear to be altered by depth of immersion. (Cf. *Biochem. J.*, 1929, **23**, 1000; 1931, **25**, 1472.) D. G. H.

Absorption of Oxygen by Tanning Materials. E. W. Merry. (*J. Inter. Soc. Leather Trades Chem.*, 1932, **16**, 239.)—The means used for testing the absorption of oxygen by various tanning materials, was the Barcroft differential manometer. The tanning materials tested were in the form of concentrated extracts:—quebracho, wattle, mimosa, mangrove, chestnut, and myrobalans; they are in the order of decreasing absorptive power, quebracho absorbing in 100 hours over 2 c.c. per grm. of dry matter, and myrobalans only about 0·3 c.c. The addition of sulphuric acid with and without hide powder, appeared to have little effect on the absorption of oxygen by a sample of American chestnut extract. The addition of iron alum increased the absorption power of the chestnut extract, and the addition of copper acetate increased it still more.

This is Part I of an extended research, and the results given should be regarded as preliminary. R. F. I.

Inorganic Analysis

Determination of Copper in Materials containing Rubber. F. Kirchof. (*Chem.-Ztg.*, 1932, **56**, 296.)—Direct ashing of substances containing rubber is tedious, and there is a danger of volatilisation of copper when the rubber contains sulphur chloride. The ashing process, preliminary to the determination of copper in the residue, has been improved, and the following treatment is suggested:—Ten to 20 grms. of the substance are cut into small pieces, and wetted with dilute nitric acid, an excess of sulphuric acid (10 to 20 c.c.) is added, the containing beaker is covered with a glass cover, and the whole is heated on a steam-bath for 1 hour. The material is transferred to a capacious porcelain crucible, the portion left adhering to the glass being dissolved in a few c.c. of acetone, and a few drops of concentrated ammonia are added to the crucible, the contents of which are then evaporated to dryness, heated with a small flame to decompose the nitro-compounds, and, finally, ashed by applying stronger heat. This process occupies 1½ to 2 hours. Copper is determined in the usual manner in the solution obtained by heating the ash with a mixture of sulphuric and nitric acids. S. G. C.

Determination of Tin in Irons and Steels. J. A. Scherrer. (*Bur. of Standards J. Research*, 1932, **8**, 309–320.)—Tin is stated to be present invariably in iron and steel, usually in amounts ranging from a few thousandths to a few

hundredths of 1 per cent. Methods for the determination of tin involving simple solution of the steel in hydrochloric or sulphuric acid under non-oxidising conditions, and titration of the solution with iodine, give erratic results; in some cases high results are obtained, owing to the consumption of iodine by compounds formed from impurities in the steel, and in other cases the results are low for reasons which are difficult to ascertain. The author recommends preliminary separation of the tin as sulphide before the iodimetric determination, but states that precipitation of the sulphide is incomplete unless the sample is completely oxidised as described below.

METHOD I, FOR MATERIALS DECOMPOSABLE BY NITRIC ACID.—*Preparation of Solution.*—To a 10-grm. sample contained in a 600-c.c. beaker, 250 c.c. of dilute nitric acid (1:4) are added. The whole is heated until the sample is completely decomposed. An excess of saturated aqueous potassium permanganate is added, and the solution is boiled for 5 minutes, after which sufficient sulphurous acid is added to dissolve the brown manganese oxide which is formed, and the liquid is again boiled for 5 minutes. Either of the following treatments are then given: (*a*) *Treatment when tungsten is absent.*—If any undissolved matter remains, it is filtered off, and the filtrate is reserved. The filter-paper (with the residue) is placed in a 500-c.c. Erlenmeyer flask, and the organic matter is destroyed by "fuming" with 10 c.c. of sulphuric acid, with the addition of nitric acid from time to time. The residue is dissolved in water, the solution is diluted to 100 c.c., and 10 grms. of tartaric acid are added; it is then neutralised with ammonia (no indicator is specified), and added to the reserved filtrate. (*b*) *Treatment when tungsten is present.*—The liquid is kept overnight, and the clear liquid is decanted and reserved. To the residue in the beaker 20 c.c. of sulphuric acid and 30 c.c. of water are added, and the whole is heated until sulphuric acid fumes are given off; 10 c.c. of concentrated nitric acid are added, the liquid is again evaporated until fumes appear, cooled, diluted to 100 c.c., and a slight excess of ammonia is added, followed by 10 grms. of tartaric acid; the solution is then neutralised and added to the reserved filtrate.

Precipitation and Determination of the Tin.—A rapid stream of hydrogen sulphide is passed for 45 minutes into the cooled solution diluted to 550 c.c., and the precipitate is filtered off after 1 to 2 hours and washed with slightly acid ammonium sulphate solution (5 per cent.) saturated with hydrogen sulphide. The paper and precipitate are heated with sulphuric and nitric acids to destroy the organic matter, the liquid being finally heated until it fumes strongly, cooled, and diluted to 100 c.c. (Where tungsten is present, 10 grms. of tartaric acid are added, followed by a slight excess of ammonia, the solution is boiled, and cooled, and 10 c.c. of sulphuric acid are added, any precipitate being filtered off and rejected.) The solution is diluted to 550 c.c., and the tin is re-precipitated with hydrogen sulphide, the precipitate being filtered off and decomposed, together with the filter-paper, as before, and the solution is diluted to 100 c.c. Fifteen c.c. of hydrochloric acid are added, any insoluble matter being filtered off and rejected. About 40 mgrms. of iron (as chloride or sulphate) are added to the solution, which is heated to boiling, a moderate excess of ammonia is added, and the precipitate of

iron and tin hydroxides is filtered off and washed with very dilute ammonia, and then with water. The precipitate is dissolved off the paper with a hot mixture of 80 c.c. of concentrated hydrochloric acid and 100 c.c. of water. The solution is diluted to 350 c.c. in a 500-c.c. Erlenmeyer flask, 10 grms. of granulated lead are added, and the flask is fitted with a rubber stopper, pierced with three holes carrying the following attachments: (1) a leading tube; (2) an air condenser consisting of a 12-inch length of glass tubing, $^{9}/_{16}$th inch in diameter, constricted somewhat at the end passing through the stopper, and fitted at the other end with a U-tube containing enough water to act as a trap; (3) a removable glass plug. A stream of carbon dioxide is passed through the apparatus, in which the solution is boiled gently for 30 to 40 minutes. The carbon dioxide supply is maintained while the liquid is cooled to 10° C., 5 c.c. of starch solution (1 per cent.) are then added by way of the air condenser, and the jet of a burette containing 0·01 *N* iodine solution is inserted in the third hole. The titration is carried to the first shade of blue; the volume of iodine solution used in a "blank" is deducted; 1 c.c. of 0·01 *N* iodine ≡ 0·0005935 grm. of tin.

METHOD II, FOR ALLOY STEELS NOT DECOMPOSED BY NITRIC ACID.—(*a*) *In the absence of tungsten.*—A 10-grm. sample is decomposed by heating with 130 c.c. of sulphuric acid (1:5); the liquid is oxidised with 25 c.c. of nitric acid (1:1), an excess of saturated permanganate is added; the liquid is boiled for 5 minutes, and the process is continued as in Method I. (*b*) *In the presence of tungsten.*—A 10-grm. sample is decomposed as in (*a*), the liquid being filtered and the filtrate oxidised with permanganate and reserved. The residue and filter-paper are decomposed by "fuming" with sulphuric acid as in Method I (*b*). The sulphuric acid residue is diluted to 100 c.c., boiled well to ensure the soluble part being dissolved, and a slight excess of ammonia, followed by 10 grms. of tartaric acid, is added. The liquid is again rendered ammoniacal, digested on a steam-bath until solution is complete, an excess of 5 c.c. of sulphuric acid is added, and the liquid is digested on a steam-bath for half-an-hour. If solution is not then complete, the insoluble matter is filtered off, the residue and filter-paper are decomposed with sulphuric and nitric acids, and the solution is united with the other. The solution is neutralised with ammonia, added to the reserved filtrate, and the precipitations and determination of the tin are carried out as in Method I. The processes are supported by the results of numerous test experiments.

S. G. C.

Determination of Vanadium in Steel according to the Potentiometric Titration Method of Thanheiser and Dickens. P. L. Blanken. (*Chem. Weekblad*, 1932, **29**, 263–264.)—In this method (*Ber.* No. 85, *Chemikerausschusses des Vereins Eisenhüttenleute*) 1 grm. of steel is dissolved, so far as possible, in 30 c.c. of 15 per cent. sulphuric acid, and (if tungsten is present) 50 c.c. of phosphoric acid (sp.gr. 1·3). A 2·5 per cent. solution of potassium permanganate is then added until the solution is strongly red, the mixture is boiled, and ferrous sulphate is added until there is no further change in colour (which becomes green if chromium is present). The solution is then diluted with 200 c.c. of 10 per cent. sulphuric acid, and 5 c.c. of potassium permanganate solution are added in excess of that

required to produce a weak rose colour. After 1 minute at 20° C. the vanadium is oxidised to the pentavalent state, the excess of permanganate being then reduced with an excess of oxalic acid. The author has now shown that if this excess is about 25 per cent., from 0·1 to 0·2 per cent. of vanadium in steel, in the presence of chromium, tungsten, molybdenum and nickel, may be determined with an error of less than 0·04 per cent. by potentiometric titration with 0·01 *N* ferrous sulphate solution, according to the equation $VO_4''' + 6H^{\cdot} + Fe^{\cdot\cdot} = VO^{\cdot\cdot} + Fe^{\cdot\cdot\cdot} + 3H_2O$. A platinum electrode is placed in a solution of the sample, which should be well stirred, and which is linked up with a *N* calomel electrode through a bridge containing a saturated solution of potassium sulphate (chlorides interfere). J. G.

Separation and Determination of Titania as Titanium Potassium Iodate. H. T. Beans and D. R. Mossman. (*J. Amer. Chem. Soc.*, 1932, **54**, 1905–1911.)—Potassium iodate produces a crystalline precipitate in acid titanium solutions; the precipitation is quantitative under the following conditions: The solution is treated with 27 c.c. of strong nitric acid, and diluted to 200 c.c. A solution of 10 grms. of potassium iodate in 100 c.c. of water and a few drops of nitric acid are slowly added to the solution during agitation After an hour's standing with occasional stirring, the flocculent precipitate should assume a crystalline form. It is filtered off by decantation and washed five times with 20 c.c.-portions of 2 per cent. potassium iodate in nitric acid (6 per cent. by volume). Filter and precipitate are returned to the beaker and stirred up with 15 c.c. of strong hydrochloric acid. After slight dilution, sulphur dioxide is passed until the brown colour is discharged. The solution is further diluted to 300 c.c., the sulphur dioxide boiled off, and the titania determined by precipitation with ammonia as usual.

A single precipitation separates titania from alumina (0·2 grm.), lime (0·1 grm.), nickel oxide (0·4 grm.), and larger amounts of magnesia. Double precipitation removes 0·35 grm. of alumina and 0·2 of lime. Larger amounts produce adsorption. In double precipitations the solution is re-treated after removal of the sulphur dioxide by boiling as described above. The separation from phosphoric acid is effective. Manganese gives a slight dark-brown deposit; the solution of the iodate precipitate is, therefore, treated with a little ammonium bisulphite, and the titania precipitated as basic acetate. Iron is completely precipitated under the conditions described; the authors remove it by Rothe's ether extraction method (*cf.* Barnebey and Isham, ANALYST, 1910, **35**, 456). Three extractions are made, the aqueous layer is freed from ether and its acidity is adjusted by an evaporation to 50 c.c., and the titanium is precipitated as iodate. The solution of the iodate precipitate is to be treated by the basic acetate process, as in the case of manganese. Zirconium in small amounts can be precipitated as iodate from 0·3 *N* sulphuric acid solution, titania being kept in solution by means of hydrogen peroxide. When the filtrate from the zirconium precipitate has been freed from hydrogen peroxide by boiling, the titania is precipitated as iodate. If more than 0·01 grm. of zirconia is present, adsorption of titania by the zirconium precipitate becomes pronounced. Vanadium also interferes. W. R. S.

Determination of Free Lime in Cement. N. A. Tananaeff and L. M. Kulberg. (*Z. anal. Chem.*, 1932, **88**, 179–183.)—The method is based on the reaction $HgCl_2+CaO+4KI+H_2O=CaCl_2+2KOH+K_2HgI_4$ in alcoholic solution, and titration of the dissolved alkali. The powder (0·2 to 0·5 grm.) is weighed into a conical flask with ground glass stopper; powdered mercuric chloride (about twice as much as is equivalent to the free lime), 15 glass beads, and 20 to 25 c.c. of absolute alcohol are added. The stoppered flask is shaken for 15 to 20 minutes; free lime is indicated by a yellow coloration (mercuric oxide). The liquid is filtered, the beads being retained in the flask; washing is effected with absolute alcohol until the mercuric chloride is completely removed (ammonium sulphide test). The washed powder is then treated with a hot potassium iodide solution in absolute alcohol, the yellow coloration being discharged. Washing is continued until a few drops of filtrate, added to a little phenolphthalein left after evaporation of the indicator on a watchglass, fail to produce a pink tint. The filtrate is diluted with 30 c.c. of cold water, and titrated with 0·1 *N* acid against methyl orange. The determination is carried out in 40 minutes. W. R. S.

Iodimetric Determination of Sulphur in Polysulphides. P. Szeberényi. (*Z. anal. Chem.*, 1932, **88**, 187–189.)—In alkaline solution, iodine oxidises sulphur according to $S+6I+4H_2O=H_2SO_4+6HI$ (1). The reaction is utilised in the analysis of polysulphide, three aliquot portions of solution being taken. In the first, the sum of monosulphide and thiosulphate is determined:

$$Na_2S_x+2I=2NaI+S_x \text{ (2); and } 2Na_2S_2O_3+2I=2NaI+Na_2S_4O_6 \text{ (3).}$$

The second portion is treated with excess of zinc or cadmium acetate solution, and the thiosulphate in the filtrate determined (3). The third portion is treated with more than enough 2 *N* alkali to yield a solution of *N* alkalinity, and an excess of 0·1 *N* iodine solution. The liquid is boiled until the turbidity caused by precipitated sulphur has disappeared; it is then cooled, acidified, and the excess iodine titrated as usual. The sulphur is oxidised as in (1), while the thiosulphate consumes eight times as much iodine as in equation (3):

$$Na_2S_2O_3+8I+10NaOH=2Na_2SO_4+8NaI+5H_2O \text{ (4).}$$

The volume of iodine consumed in the titration of the third portion, less eight times the volume consumed in the titration of the second portion, gives the measure of the total sulphide sulphur; the total sulphide sulphur, less monosulphide sulphur (2), gives polysulphide sulphur. W. R. S.

Determination of Silica by Means of Perchloric Acid. F. W. Meier and O. Fleischmann. (*Z. anal. Chem.*, 1932, **88**, 84–92.)—For the decomposition of acid-soluble silicates (Portland cement, blast furnace slag, water-glass) the following procedure is recommended: The substance is finely ground in agate, and 1 grm. weighed into a conical flask provided with a reflux condenser (ground-glass joint). It is made into a cream with 10 c.c. of water, and heated with 15 c.c. of perchloric reagent, containing 60 per cent. of perchloric acid and 7 per cent. of concentrated hydrochloric acid (sp.gr. 1·19) on a sand-bath, until white fumes are given off. The cooler is then inserted, and heating continued for 15 minutes. The

hot solution is diluted with 70 c.c. of 10 per cent. hydrochloric acid, digested for 5 minutes at 90° to 100° C., and filtered hot; the precipitate is washed with hot 10 per cent. hydrochloric acid, finally with a little water, and ignited as usual. The determination requires one hour. W. R. S.

Physical Methods, Apparatus, etc.

Refractometric Determination of Organic Acids. G. Allard. (*Bull. Soc. Chim.*, 1932, **51–52**, 372–376.)—If the volume of a 0·99 *N* solution of lead acetate, added to a solution of oxalic or malonic acid, is plotted against the refractive index (*n*) of the mixture, two straight lines are obtained corresponding with the decrease and increase in *n* with decrease in concentration of acid and increase in concentration of lead acetate, respectively, and intersecting at a point corresponding with the amount of the latter required to precipitate all the organic acid present. Optimum results, corresponding with the most acute angles between the lines, are obtained for 0·25 to 0·0025 *N* acids, and the solubility of the lead salts is sufficiently small to reduce the error, as a rule, to below 2 per cent. A suitable working-volume is 20 c.c., the reagent being added from a micro-burette so as to avoid errors due to a large change in volume. Mixtures of oxalic and malonic acids may be titrated, with errors of 0 to 3 and 6 per cent., respectively. The graph in such cases consists of 4 straight lines corresponding, in succession, with precipitation of lead oxalate, soluble lead malonate (a short portion), precipitation of lead malonate, and an excess of lead acetate, respectively. The Zeiss immersion-refractometer is recommended, and the temperature should be controlled to within 0·2° C. or the readings corrected for temperature accordingly. J. G.

Restoration of Museum Objects. A. Scott. (*J. Soc. Arts*, 1932, **80**, 488–494.)—Since the last of the three published Reports on the restoration of museum objects (ANALYST, 1927, **52**, 81) new substances have been employed, and more severe tests as to permanence have been applied. The types of deterioration dealt with include the following:

CRYSTALLISED SALT IN STONE.—To preserve stone which has been buried in moist soil containing soluble salts it is necessary to remove these salts. Soaking the object in water only results in the resulting solution of salts being immediately drawn further into the porous body of the dry stone. The most effective method is to apply to the surface of the object wet blotting-paper pulp containing only sufficient water to dissolve the salts and retain them, and then to allow the pulp to dry from the outside only. For the removal of crystallised salts from cuneiform tablets, three successive coats of celluloid solution were applied, and the tablets were then placed in relays of distilled water, with the result that the salt was dissolved and diffused into the outside water.

GREASE STAINS.—These may often be removed by means of pyridine.

REMOVAL OF "FOXED" MARKS.—The brown stains produced by the growth of mould fungi can be removed by treatment with a 2 per cent. solution of chloramine-T, without affecting any of the ordinary pigments used in water colours. Pictures

thus treated have been exposed to strong daylight for five years without any change of the tints being detected.

"Bronze Disease" of Copper.—The deterioration of the surface of copper objects which have been buried in the soil is known as the "bronze disease"; it is due to the action of chlorine, generally derived from sodium chloride in the soil. The best method of preserving the patina, consisting of hard stannic oxide coloured by copper compounds, is to soak the object in sodium sesquicarbonate solution. This gradually removes the chlorine without attacking the patina, and the object is then thoroughly washed with water. In more aggravated cases it may be necessary to strip off all compounds, *e.g.* by soaking in a 3 per cent. solution of citric acid, or even to treat the object "electrolytically" with zinc and sulphuric acid or caustic soda solution.

Treatment of Friable Leather.—A brittle roll of Ancient Egyptian leather was rendered flexible by coating it with three coats of a 2·5 per cent. solution of celluloid in such a way that the various folds did not adhere together, and, when it was thoroughly dry, applying a 5 per cent. solution of celluloid. It could then be unrolled and pressed flat under a sheet of glass.

Fourteenth Century Glass of Wells Cathedral.—A peculiar coating on the windows in the Lady Chapel of Wells Cathedral was found to consist of calcium sulphate in small nodules. The sulphuric acid had originated from the combustion of the gas used for lighting the cathedral, which had condensed on the windows, where it had combined with the fine powder derived from the soft limestone with which the floor was paved.

Removal of Tar from Marble.—A white marble bust which had been exposed to the smoke from a fire was covered all over with black tarry particles. To prevent the solution of the tar in a solvent from sinking into the marble, it was necessary to use an emulsion of benzene, dilute aqueous ammonia solution, and methylated spirit. When this was applied with a tuft of cotton wool, the drops of benzene picked up the particles of tar, whilst the water, assisted by the methylated spirit, penetrated the uncovered marble, thus keeping out the benzene solution of tar. On then wiping the surface the bust was left as white as it was originally.

Marble Stained with Red Ink.—Every trace of the red colour was removed by means of chloramine-T without roughening or injuring the polished marble surface of a bust.

Reviews

Annual Reports on the Progress of Applied Chemistry for the Year 1931. Vol. XVI. Published by The Society of Chemical Industry. Price, members 7s. 6d.; non-members 12s. 6d.

Everyone interested in the chemical aspect of industry awaits with impatience the Annual Reports issued by the Society of Chemical Industry. All concerned are to be congratulated on the early publication this year and on the general high

standard of the various articles of which the volume consists. These articles or sections are twenty-four in number, and cover effectively the whole range of chemical activity from fuels to food, from soils to sanitation, from gas to glass, from metals to medicinal substances, and each review of the year's work in one particular section is written by a specialist in that branch. Naturally it does not always follow that the specialists as such are capable of presenting to the waiting world of chemists a balanced record of the progress of the last twelve months. In fact, as specialists, they may be biassed to one way of thinking, and therefore may not give due prominence to suggestive work at variance with their own particular views. It is a difficult task to present a short synopsis of the vast amount of work which appears during any one year, and the method of presentation varies. At one end of the scale is the descriptive article, with a more or less serious attempt to sift the grain from the husk; at the other end the index type, where the reviewer is content to give a whole list of references with little criticism or discernment. Both methods have their advantages, and, as would be expected, the articles published in the volume under review are generally a blend with a bias towards one type or the other. Whether we agree with the method pursued or not, it can certainly be said that the volume, running to over 600 pages (with efficient name and subject indexes of more than 50 pages), is an invaluable one, and should certainly be in the hands of every chemist, not only the industrial chemist, but also the so-called "pure" chemist, for the boundary between them becomes progressively thinner and less distinct.

L. H. LAMPITT.

APPLIED CHEMISTRY. By C. K. TINKLER, D.Sc., F.I.C., and HELEN MASTERS, B.Sc. Vol. II (Foods). Second Edition. Pp. 284. London: Crosby, Lockwood & Son. Price 15s.

This is the second edition of the volume, which was published first in 1925. The changes are slight, but important; they comprise adequate references to the regulations with regard to preservatives, some references to recent analytical work, and some slight modifications which were suggested in reviews of the first volume.

In reviewing this book the writer feels that he cannot express his opinion better than by the following abstract from his original review:

"This volume is written for students of household science and public health. It is described in the preface as dealing with 'certain branches of the chemistry of food and with the interpretation of the analytical results obtained,' but its scope is not so limited as this description might suggest, as is shown by the following list of contents:—Milk, 31 pages; Edible Oils and Fats, 33 pages; Carbohydrate Foods, 63 pages; Raising Agents, 29 pages; Meat, Meat Extracts, etc., 19 pages; Vinegar, Fruit Juices and Vegetable Acids, 17 pages; Beverages, 13 pages; Preservation of Food, Condiments, etc., 36 pages; The Calorific Value of Foods, 12 pages.

"There can be no doubt that the book adequately fulfils its purpose, for it is obvious throughout that the authors have desired not only to present the necessary information, but also to ensure a thorough understanding of the chemical principles involved. This latter is such a feature of the book that, although it is written expressly for a special university course, it might well be read with profit by students who need a fuller knowledge of the chemistry of food. Excellent

examples of the educational value of the book are the explanation of the iodine value of an oil or fat, pages 42 to 46; Chapter IV, on Raising Agents; Chapter VI, on Vinegar, etc.

"The analytical methods given are those usually employed in routine analysis, and are well described. The necessary calculations are particularly carefully explained, though the extreme attention to detail in some of these suggests rather poor arithmetical ability on the part of the students.

"Cocoa and Chocolate, pages 200 and 201, receive meagre treatment, and no analytical work is described.

"A description of a method of determining the amount of stalk in tea might have been included as being of use to students of household science; also, a method for estimation of chicory in coffee mixtures might have been given.

"The volume bears evidence throughout of careful and considered compilation, and is of real educational value."

E. B. HUGHES.

AN INTRODUCTION TO BIOCHEMISTRY. By ROGER J. WILLIAMS, Ph.D. Pp. xiv+501. London: Chapman & Hall, Ltd. 1932. Price 21s.

The idea which inspired the writing of this book is a good one—namely, that a knowledge of biochemistry is to-day essential for all students of chemistry, and that a course in the subject should, therefore, find a place in every chemical curriculum. The difficulties of drawing up a well-balanced outline of biochemistry are, however, great, and it cannot be claimed that Professor Williams has succeeded in dealing with them. Success in presenting a wide view of a subject depends on the ruthless removal of confusing detail, and in several sections of this book the pruning knife has not been applied with sufficient vigour.

The book is divided into sections dealing with the composition of organisms, their nutritional requirements, the mechanisms used by them for promoting and regulating chemical change, and three sections on metabolism. The latter are undoubtedly the best part of the book, and are worth attention. There is also an addendum on suggested laboratory experiments, which the author probably finds useful to his own classes, but which will not supersede the recognised standard text-books on this side of the subject, and which appears to be a little out of place. Though much detailed biochemical information is offered, few references are given. The book, therefore, cannot be used as a work of reference by the trained chemist. It appears more than likely that the chemist in training will find parts of it very confusing, and, moreover, will form the erroneous impression that biochemical research is carried out almost exclusively in North America.

The printing is good, but the price is excessive.

DOROTHY JORDAN LLOYD.

THE GLYCOSIDES. By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S., and K. F. ARMSTRONG, B.A., B.Sc. Pp. vii+123. London: Longmans, Green & Co. 1931. 12s. 6d.

The section on glucosides in the Simple Carbohydrates and the Glucosides has now been re-written and brought up-to-date, and appears as a separate volume in the well-known series of monographs on biochemistry. The term "glycoside" is stated to be the new official name for the large number of substances containing

sugars linked to one or more other compounds: "glucoside" is now the specific name used for those glycosides, the sugar constituent of which is glucose. The non-sugar parts of the glycosides are referred to as "aglucones," a term originating with the Japanese chemists. The complex and diverse nature of the aglucones is illustrated by the headings of the chapters: Natural Glycosides (Phenols, Hydroxyanthraquinones and Hydroxycoumarins); Glycosides of the Soluble Plant Pigments (Anthoxanthins and Anthocyanins); Glycosides with Physiological Action (Digitalis, Strophanthin, Saponin); Other Natural Glycosides (Mustard Oils, Cyanophoric Glycosides, Nucleosides, Indican, Pentosides); Synthetic Glucosides; Uronic Acids.

The functions of glycosides in plants are discussed, and it is pointed out that no one explanation will cover the activities of all the members of the group. According to the authors, aglucones in the free state oxidise, polymerise and undergo other changes, but are stable when linked to sugar molecules. They thus remain dormant until liberated by the appropriate enzyme, when they become the hormones or activators of plant cells. In an interesting discussion on glycosides and animal nutrition, it is suggested that this stimulating action of the constituents of glycosides also determines, to some extent, the nutritive value of herbage. The non-sugar constituents can frequently be detected with certainty, and also estimated quantitatively, and glycosides are, therefore, likely to become of importance analytically.

The final chapter is devoted to the utilisation of carbohydrates in plants, the main points reviewed being the protection afforded to the plant against low temperatures by the presence of carbohydrates, and the changes in the nature and amounts of carbohydrates during the growth, ripening and storage of fruits.

To all those concerned with plants and plant materials this concise monograph, with its extensive bibliography, will be invaluable. H. PHILLIPS.

RECENT APPLICATIONS OF ABSORPTION SPECTROPHOTOMETRY. Compiled by the Advisers and Staff of A. Hilger, Ltd. Pp. 44. London: A. Hilger, Ltd. 1932.

This small volume is intended to serve as a supplement to *The Practice of Absorption Spectrophotometry with Hilger Instruments*, and consists of a bibliography of the principal papers published in this country, in America and on the Continent during the last ten years.

It is divided into four parts, each of which is sub-divided according to the portion of the spectrum employed, the subject treated of, or the title of the publication in which the paper appeared.

Part I, by Dr. W. R. Brode, gives the titles and a brief summary of 137 papers on physics, physical, inorganic, organic, and biological chemistry and industrial colour measurement, published between 1922 and 1927. Part II provides a similar selection of 211 papers (excluding those on biochemistry, which have been relegated to Part IV) appearing between 1927 and 1931. Part III, by Dr. S. Judd Lewis, comprises a supplementary list of publications in the *Berichte, Biochemische Zeitschrift, Biochemical Journal,* and the *Proceedings of the Royal Society*; while Part IV is devoted mainly to papers on biochemistry and pathology, over half of

these dealing with the important subject of vitamins and allied substances. The publishers have shown commendable enterprise in the publication of such a well-produced monograph, which will be widely welcomed by workers in many branches of science, by whom the utility of such a compilation will be greatly appreciated.

T. J. WARD.

INDUSTRIAL CHEMICAL CALCULATIONS. By O. A. HOUGEN, Ph.D., and K. M. WATSON, Ph.D. Pp. 502. London: Chapman & Hall, Ltd. 1931. Price 28s. 6d.

This book is concerned mainly with the indefinable borderland between applied physical chemistry and engineering, and should, therefore, appeal both to engineers interested in chemistry and to chemists whose work brings them into contact with engineering problems. In addition, it should prove very useful to the student of chemical engineering, although the fully-qualified chemical engineer will probably find it rather elementary.

The authors start from fundamental principles, such as the compounding of mixtures and stoichiometry. This leads to a consideration of the kinetic theory, to which considerable attention is devoted, in spite of its limitations. The authors recognise the existence of these limitations (although, unfortunately, they do not state them), but believe, rightly, that the theory provides a clear-cut mental picture of the mechanism of changes in energy and lends itself to simple mathematical treatment. Gaseous mixtures, vaporisation, crystallisation and adsorption are then considered, and, except for short chapters on distillation and chemical equilibria, the remainder of the book is devoted to thermo-physics and thermo-chemistry (including weight- and heat-balances and fuels). The section on coal should be of particular interest to the analyst.

In each chapter the procedure is to outline, in simple terms, the fundamental physico-chemical theory, and then to demonstrate its mathematical treatment. Worked examples and numerous problems applying to a great variety of industries illustrate the principal points. The authors have spared no pains to clarify their mathematical working by labelling each individual step, and, if this has added considerably to the length of the book, it has the advantage that the non-mathematical reader need not be frightened by the title. Arithmetical short-cuts have been purposely avoided, and even if the desirability of such a policy is admitted, there is, in the reviewer's opinion, no excuse for the omission of a chapter on other aids to rapid calculation. It is surprising, for example, how many chemists are strangers to the slide-rule, and no chemical engineer can be said to have completed his education without a knowledge of nomography. A few pages on nomogram-construction, illustrated by some typical examples, would have added considerably to the value of the book.

Apart from this, there is little other than praise for the book. It is written in a style which will appeal to English readers, and it is well-produced. The mathematics are sound, and those problems tested did not give impossible results. The use of B.T.U. (instead of B.Th.U.) for the British Thermal Unit does not distinguish it from the Board of Trade Unit, but this is one of few misprints, and is, possibly, excusable in a book of American origin.

JULIUS GRANT.

SOAP. By W. H. SIMMONS, B.Sc. (Lond.), F.I.C. Pp. ix+134. London: Sir Isaac Pitman & Sons, Ltd. Price 3s.

This little volume, which has recently appeared in the form of a third edition, gives a succinct and very readable account of the various features connected with soap manufacture and glycerine recovery. Writing for those not necessarily familiar with chemistry, Mr. Simmons has succeeded in the very difficult task of reconciling scientific accuracy and clarity with the use of perfectly simple English, and has done this without evading many specific terms, both chemical and technological, which are pertinent to the subject. He introduces technical phraseology in such a manner that one feels that the reader must subconsciously realise not only its meaning, but its *utility*. This last-mentioned virtue seems frequently to be overlooked by those well-meaning individuals who love to rate chemists for writing in a "language" which the uneducated cannot understand; admittedly there are two extremes in the matter, but Mr. Simmons shows that both can be avoided.

The technical descriptions are clear and cover practically the whole of the art of soap-making; of course, the treatment cannot be exhaustive within a matter of 130 small pages, but it is remarkable how much has been collected together in this limited space. One believes that the book will be useful, for example, to many readers of this journal who wish to acquire a rapid acquaintance with the conditions of manufacture of different types of cleansing material. Most attention is devoted to household, toilet, shaving, soft and textile soaps; soap powders, dry soaps, etc., are briefly dealt with, and possibly might, with advantage, have received a little more space. Similarly, distilled glycerine is rather briefly handled by comparison with the evaporation processes for the production of crude glycerines, which are very well explained.

In one or two minor points the author's views are, perhaps, open to question. Thus the hydrogenation processes are said (p. 7) to lead to a "depletion of the soap-makers' resources" by diversion of soap-making raw materials into fats of edible quality; but surely, on balance, the soap-producer has gained as much, or more than, the edible-fat manufacturer, since a number of oils, especially whale oil, which were formerly useless, or only usable as "soft" oils, have by this means been converted into potential sources of fats of the hardness of tallow. From p. 26 it might be concluded that alkaline silicates are made by concentration of neutral silicate solutions to 140° Tw., and it would possibly have been better to make it clear that the composition of the two grades is controlled by the proportions of soda-ash and sand in the original melt. The present book probably retains traces of earlier editions when it is suggested, here and there, that glycerine is the most valuable product of the soap factory; certainly this was true ten or fifteen years ago, but times have changed since then!

The short section on "commercial valuation of soap" (pp. 106–107) is of especial interest to the analyst. It may be doubted whether Mr. Simmons's desire for a "legal definition of what is soap" would prove to be in the best interests of the consumer; so many classes of soap, different in cost but with definite uses, are on the market that, as indeed he points out, account must be taken of a number of factors in considering the specification for any given soap. T. P. HILDITCH.