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THE ANALYST

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NORTH OF ENGLAND SECTION

THE Fifth Summer Meeting was held at the Craigside Hydro Hotel, Llandudno, from June 22nd to 25th. The attendance was forty-seven, including many ladies.

The Chairman (Professor W. H. Roberts) presided, and among those present were the following:—the President (Mr. John Evans); Past-Presidents (Dr. J. T. Dunn, accompanied by Mrs. Dunn, and Mr. F. W. F. Arnaud with Mrs. Arnaud); Hon. Treasurer (Mr. E. B. Hughes); Editor of the ANALYST (Dr. C. A. Mitchell); Mr. A. L. Bacharach with Mrs. Bacharach, Dr. H. E. Cox, Mr. E. M. Hawkins and Miss Elliott.

On Saturday morning a lecture, illustrated by lantern slides, was given by Professor A. P. Laurie, entitled "Old Masters and Modern Forgeries." Dr. Laurie gave an account of the most recent apparatus and methods, involving the use of infra-red and ultra-violet rays, etc., employed in the examination of pictures. The Vice-Chairman (Mr. A. R. Tankard), who presided in the temporary absence of the Chairman, extended a cordial welcome to the lecturer and to all attending the meeting, especially those from the south. A vote of thanks to Dr. Laurie was proposed by the President and seconded by Mr. Arnaud.

On the motion of Dr. Dunn seconded by Mr. R. W. Sutton, a resolution was unanimously passed, expressing the cordial greetings of the Section and affirming its continued loyalty to the Council of the parent Society.

The meeting received with great pleasure the announcement that the President (Mr. John Evans) was about to receive the degree of M.Sc. (*honoris causa*) from the University of Sheffield and offered him their hearty congratulations.

A telegram was sent to Dr. J. A. Voelcker conveying the hearty congratulations of the Meeting on the attainment of his eightieth birthday.

Mrs. W. H. Roberts presented all the ladies with a Victorian posy and was thanked, on their behalf, by Mrs. J. T. Dunn.

The President proposed a vote of thanks to the Hon. Secretary (Mr. J. R. Stubbs) for his work in arranging the Meeting.

On Sunday afternoon the party proceeded by motor through the Snowdon district to Bettws-y-Coed, where tea was taken.

The Determination of Free Silica in Coal-Measure Rocks

By A. SHAW, B.Sc.

(*Read at the Meeting, May* 2, 1934)

In silicate rock analysis no great difficulty is experienced in determining the amount of total silica present; to differentiate between the silica present in the free state and that combined as silicates is, however, a problem of much greater difficulty. In the past the problem has been attacked in various ways, but the only method which has met with any degree of success is that evolved by Lunge,[1] Mellor[2] and others, based on the "rational analysis" principle. The method appears to have been used mainly for the determination of free silica in clays, and has met with much adverse criticism on the ground that the results obtained were not in agreement with those calculated from the ultimate analysis. Although neither of these methods was capable of giving results of great accuracy, no further work appears to have been done on the subject. Recently, however, in consequence of the research being carried out on the incidence of silicosis amongst coal miners, it became increasingly important that some reliable means of estimating the free-silica content of rocks and shales should be available; and, with this object in view, investigations were commenced in the Mining Research Laboratory, Birmingham, to compare the various methods in use. Reference to existing literature showed that the methods capable of application to coal-measure rocks were that of calculation from the ultimate analysis, and two modifications of the rational analysis. In addition, Mr. H. V. Thompson, of North Staffordshire Technical College, and Professor Sollas each suggested a method that might be adapted to the determination of free silica in shales. Although neither of these two suggested methods proved capable of general application, a short description of each may be of interest.

THOMPSON'S METHOD.—This is based on the fact that quartz (sp.gr. 2·66) is converted into tridymite (sp. gr. 2·28) when heated under molten sodium chloride for forty-eight hours.[3] The loss on ignition of the sample is first determined, and then the density of the ignited material. After conversion of the quartz into tridymite, the density of the material is again determined. If s_0 and s_1 represent the densities of quartz and tridymite, respectively, d_0 and d_1 the densities of the material before and after conversion of the quartz, and p the percentage loss on ignition, then the amount of quartz present in the original material can be shown to be

$$\frac{(100 - p)\, s_1 s_0\, (d_0 - d_1)}{d_0 d_1\, (s_0 - s_1)} \text{ per cent.,}$$

assuming

(i) That, on ignition, none of the quartz becomes combined with the remainder of the material.

(ii) That fusion under molten sodium chloride has no chemical or physical effect on the materials present other than quartz.

(iii) That the free silica is present in the form of quartz with a density approximately 2·66.

Samples of Bedlington shale, Scotch Whinstone, and dust from the Ooregum Mines, Mysore, were subjected to the above treatment, with the result that in each case the sample increased in weight after being heated with molten sodium chloride, showing that combination had taken place. It was concluded, therefore, that the method was not generally applicable, and this conclusion was afterwards confirmed by Thompson, who found that kaolin combined with sodium chloride under the experimental conditions. The residue of quartz, felspar, etc., from the rational analysis of a shale, tested by Thompson's method, gave a result in good agreement with that obtained by correcting for the felspar present in the usual way, showing that the method may be applied in exceptional cases where little or no combination takes place. The tests showed, however, that there was little possibility of the method being successful when applied generally to coal-measure rocks.

SOLLAS'S METHOD.—The method suggested by Professor Sollas consists in the determination of the sp.gr. of the minerals present in the rock and their separation by float and sink tests, the actual procedure being as follows:

The sample is crushed to pass a 30-mesh sieve, washed by sedimentation to remove fine particles and dried, the sp.gr. of the constituent minerals being determined by means of the liquid diffusion column. This is prepared by placing in a long test-tube small amounts of mixtures of bromoform and benzene of varying sp.gr., the heaviest fraction first, and the others in order of decreasing sp.gr. On standing, diffusion takes place until the sp.gr. of the liquid varies fairly uniformly over the length of the tube, *i.e.* the sp.gr. at any point in the liquid is dependent on the depth. The dried sample is introduced into the tube, a little at a time to prevent the grains clogging, and the tube is allowed to stand for a short time. The mineral grains sink until they reach a point where the sp.gr. of the surrounding liquid is equal to that of the grains, and at these points the mineral particles float. By the introduction of various minerals or glass beads of known sp.gr. into the tube, a graph can be drawn showing the sp.gr. of the liquid at any point, and from this and the relative positions of the various bands of particles the sp.gr. of the mineral constituents of the sample can be obtained.

Separation of any particular mineral is then effected by immersion of a fresh portion of sample in a liquid of suitable sp.gr., whereby all heavier minerals are removed. This is followed by a further separation of all light minerals. Although this method has been used successfully by Sollas for the analysis of coarse-grained rocks, it was obvious that greater difficulty would be experienced in its application to the analysis of such fine-grained rocks as coal-measure shales. Moreover, the possibility of the presence, in such shales, of soda-lime felspars having specific gravities approximating to that of quartz would add to the difficulty of effecting a complete separation. In order, however, to obtain information regarding the accuracy of such separation, several tests were made on artificial mixtures of quartz and orthoclase. The results showed that, although good separations could be obtained with mixtures ground to pass a 30-mesh sieve, the error in the case of finer mixtures was of the order of 10 per cent. As shales would have to be ground to pass a 60-mesh sieve, at least, in order to effect any appreciable separation of the mineral grains, it was obvious that the method could not be applied to the separation of quartz from shales.

RATIONAL ANALYSIS.—The two methods suggested by Thompson and Sollas having proved to be inapplicable, attention was then turned to the much-criticised rational analysis. The many variations of this method in existence differ only in experimental procedure, but the principle is the same, *viz.* the attempt to remove from the sample under analysis all minerals except the quartz. The various minerals present are decomposed by suitable treatment with acids (sulphuric and hydrochloric), and the products of decomposition are removed by solution in water and Lunge solution (100 grms. of crystallised sodium carbonate and 10 grms. of sodium hydroxide in 1 litre of solution). Unfortunately, however, the decomposition is seldom complete, with the result that the residue obtained after such treatment contains not only the quartz, but also varying quantities of undecomposed silicates. A correction is usually made for the presence of these undecomposed minerals, by assuming them to be orthoclase, the amount being calculated from the alumina present in the residue. This correction, which is seldom accurate, has given rise to a certain amount of criticism, but, in view of the results obtained from the analysis of numerous shales in the Mining Research Laboratory, it would appear that the error introduced is negligible in most cases. It is obvious, however, that the correction will give rise to large errors if the sample contains large amounts of undecomposable silicates with an alumina-content differing greatly from that of orthoclase; for this reason alone the method cannot be applied indiscriminately to all rocks. This correction is by no means the only source of error, but before attempting to estimate the magnitude of the errors, comparative tests were made to decide which variation of the rational analysis should be adopted, the two methods chosen being a modification of that of Lunge and Millberg[1] and that of Selvig,[4] with one or two minor alterations.

The modified method of Lunge and Millberg is as follows:—

Mix about one grm. of the finely-powdered material in a platinum dish with 40 ml. of distilled water and 10 ml. of concentrated sulphuric acid. Cover the dish with a clock glass and heat until fumes are given off. Allow fuming to continue for 15 minutes, set aside to cool, dilute with water and allow the mixture to settle. Decant the clear liquid through a filter, retaining as much as possible of the insoluble matter in the dish. To the residue add 1 ml. of concentrated hydrochloric acid and a little water, boil, allow the mixture to settle, decant through the filter and wash. A further extraction with hydrochloric acid may be necessary if much iron is present. Next add 15 ml. of a 10 per cent. solution of sodium carbonate crystals, boil, dilute and decant. Repeat the extraction with another 15 ml. of sodium carbonate solution, then transfer the residue to the filter, wash with water and dilute hydrochloric acid, and, finally, with water. Transfer the residue to a platinum crucible, ignite and weigh. The residue is quartz and undecomposed silicates. The proportion of the latter may be approximately obtained from the amount of alumina present, on the assumption that the undecomposed silicate is orthoclase. The alumina is determined by treating the residue with sulphuric and hydrofluoric acids, evaporating until fumes of sulphuric acid are freely evolved, extracting with water and precipitating the alumina in the usual manner. The weight of alumina, multiplied by 5·41, gives a figure for the felspar which, when deducted from the previous weight of quartz, felspar, etc., gives the proportion of quartz.

The method finally adopted in the Mining Research Laboratory, Birmingham, was that of W. A. Selvig, with one or two minor modifications, the details being as follows:—Five grms. of the sample, ground to pass 60-mesh I.M.M., are mixed with 300 ml. of dilute hydrochloric acid (2·5 per cent. by vol.), and heated to boiling in a deep porcelain dish of 1300 ml. capacity. The dish is allowed to stand for 2 hours, or until the material has settled, and the clear liquid is syphoned off. It is advisable to have a tap or pinch-cock in the syphon tube to reduce the rate of flow towards the end of the operation; if the syphon is clamped so that the end of the short limb is adjustable in the liquid, it will be found possible to remove practically the whole of the solution without disturbing the solid material. The residue is stirred with 100 ml. of water, 100 ml. of sulphuric acid (1 : 1 by vol.) are added, and the mixture is boiled, with frequent stirring, until acid fumes are freely evolved. The temperature of the solution should not rise above 200° C., and the total time of evaporation should be approximately 45 to 60 minutes. The dish is allowed to cool for 30 minutes, and its contents are diluted with a litre of water, well stirred and allowed to settle. The clear solution is syphoned off, and the residue is treated with 100 ml. of water and 100 ml. of the sulphuric acid and evaporated once more. After dilution, and settling and syphoning off the solution, the residue is neutralised with Lunge solution. If the amount of acid liquid remaining in the dish is large (20 ml. or more), 50 per cent. sodium hydroxide solution should be used for neutralisation, to prevent excessive dilution of the Lunge solution in the following operation. Three hundred ml. of Lunge solution are then added, and the liquid is heated to boiling, with frequent stirring. After standing for two hours the solution is syphoned off, and the residue is boiled for 5 minutes with 500 ml. of concentrated hydrochloric acid, diluted to one litre, and allowed to settle. The acid solution is syphoned off, the residue is neutralised with Lunge solution or 50 per cent. sodium hydroxide solution, 150 ml. of Lunge solution are added, and the liquid is heated to boiling. After standing for two hours, the Lunge solution is syphoned off, and the residue is boiled for five minutes with 200 ml. of concentrated hydrochloric acid. Two hundred ml. of water are then added, and the liquid is filtered through a Whatman No. 40 filter. The residue is transferred to the filter, washed twice with hydrochloric acid (1 : 3 by vol.) and then with water, until the washings are free from chlorides, and, finally, ignited to constant weight in a tared platinum crucible. To the ignited residue are added 5 ml. of water, 5 to 10 drops of concentrated sulphuric acid and 15 ml. of hydrofluoric acid, and the resultant liquid is evaporated on a hot plate until sulphuric acid fumes are evolved. The evaporation is repeated with two further quantities of hydrofluoric acid, heating being continued during the final evaporation until sulphuric acid fumes are *freely* evolved, to ensure complete removal of fluorine, which would interfere with the determination of alumina in the residue. The contents of the crucible are extracted with water, and the solution is filtered. The alumina in the extract is then determined in the usual way by precipitation with ammonia, methyl red being used as indicator to avoid excess.[5] The weight of alumina, multiplied by 5·41, gives the equivalent weight of potash felspar, and this, subtracted from the weight of the ignited residue previously determined, gives the amount of quartz or free silica in the sample.

The above method differs from that of Selvig in the use of a syphon in preference to decantation, the grinding of the sample to pass 60-mesh I.M.M. instead of 200, and the removal of silica from the residue by evaporation with hydrofluoric acid instead of by fusion with sodium carbonate and separation of the silica by evaporation to dryness with hydrochloric acid.

Four samples were analysed by each method, the results being shown in Table I. Although the results obtained with two samples agreed well, those obtained with samples R.121 and R.122 differed greatly. Duplicate analyses by Selvig's method gave consistent results, whereas those obtained by the Lunge method showed great variations. As a further check, Dr. Francis supplied results of analyses of two of the samples carried out in the Government Laboratory by Lunge's method and by Selvig's method. The results, also given in Table I, bear out the fact that Selvig's method is capable of giving consistent results, whilst that of Lunge is not.

TABLE I

COMPARISON OF THE MODIFIED LUNGE AND SELVIG METHODS FOR FREE SILICA

	Free SiO_2	
Sample	Lunge method Per Cent.	Selvig method Per Cent.
R.121	52·6	26·1
	50·6	25·8
	48·0	28·2*
	38·2*	25·2*
R.122	36·9	21·3
	46·2	20·1
	43·3	21·9*
	44·8*	19·3*
R.123	4·0	4·5
	29·8*	4·5
"Greys"	71·0	71·4
	68·7	71·1

* Figures supplied by the Government Chemist.

As it was apparent that Lunge's method was liable to give rise to large errors, a test analysis of pure china clay was made by this method, silica and alumina being determined in the various acid and alkali extracts. Table II shows the amount of silica and alumina in the different extracts, compared with the ultimate analysis of the kaolin. It will be seen that, whilst all the alumina had been extracted (which would indicate complete decomposition of the kaolin), only half the silica had been removed, the remainder passing on to the residue, and so giving rise to a high figure for the quartz present. The actual result obtained was roughly 20 per cent. of free silica by this method, whilst that of Selvig gave a result approximately nil. It was evident from this that the alkali treatment in Lunge's method was insufficient to remove the silica that resulted from the decomposition of the kaolin, and that the high results obtained in the case of samples R. 121 and R. 122 were probably due to this cause. As a result of these tests, it was decided to adopt Selvig's method, and investigations were begun with a view to estimating the magnitude of the errors which might arise.

TABLE II

SILICA- AND ALUMINA-CONTENTS OF ACID AND ALKALI SOLUTIONS OBTAINED DURING RATIONAL ANALYSIS OF KAOLIN BY THE LUNGE METHOD

	Silica Grm.	Alumina Grm.
Sulphuric acid extract ..	0·0030	0·1798
Hydrochloric acid extract ..	0·0031	0·1892
Lunge solution extract ..	0·2334	0·0034
Total extracted	0·2395	0·3724
Ultimate analysis of kaolin ..	0·4833	0·3678

From a consideration of the analytical procedure given above it will be seen that the chief sources of error are:—(i) Mechanical loss of quartz through syphoning; (ii) loss of quartz by solution in alkali; (iii) incomplete decomposition of minerals present other than quartz; (iv) incomplete removal of the products of decomposition.

Rational analyses of samples of quartz showed that mechanical loss and loss due to solution in alkali amounted to 1·2 per cent. with quartz ground to 60-mesh I.M.M., and to roughly 6 per cent. with quartz ground to 200-mesh. The effect of the solvent action of the alkali alone was determined by treating quartz and several shale samples with Lunge solution as in the rational analysis procedure, the extract being filtered and the dissolved silica determined by evaporation with sulphuric acid in the usual way. Table III shows that the maximum amount of silica extracted from the shales is 1 per cent., and that with quartz through 200-mesh, only 2 per cent. is dissolved from a 5-grm. sample. As only 6 per cent. is dissolved from 0·5 grm. of quartz it would appear that only the finer quartz particles go into solution, and that when shales are ground to pass 60-mesh I.M.M. the amount of fine quartz produced is insufficient to cause any large error due to solution in alkali. The error may have been appreciable when the method was used for the rational analysis of clays, the average diameter of the particles of which is less than 0·002 mm., but with coal-measure rocks and shales the grain size is greater than 0·001 mm., and, as a result, the solubility of the quartz particles in Lunge solution is inappreciable. Moreover, if desired, a correction for this error may be applied by making a solubility test of the sample in Lunge solution.

The third source of error, *viz.* incomplete decomposition of minerals other than quartz, is always present, for the residue obtained from the rational analysis never consists entirely of quartz. A number of minerals were, therefore, subjected to the rational analysis treatment in order to obtain information regarding the amount of decomposition that takes place under such conditions. As it was manifestly impossible to check the action of the rational analysis treatment on all known minerals, only those minerals that are likely to occur in shales in any great amount were tested. Table IV shows the amount of decomposition that takes place when various minerals are subjected to the method of rational analysis, together with a partial analysis of the minerals before and after decomposition.

TABLE III

EFFECT OF LUNGE SOLUTION ON QUARTZ AND VARIOUS SHALES

	Free silica Per Cent.	Silica dissolved Per Cent.
Quartz (5 grms., 200-mesh)	100	2·07
Quartz (0·5 grm. 200-mesh)	100	6·2
Llay Main "Hard rock," 60-mesh ..	44·6	0·64
,, ,, White shale ,, ..	20·2	0·69
,, ,, Grey shale ,, ..	27·5	1·03
,, ,, Floor ,, ..	22·1	1·04
,, ,, "Hard rock" ,, ..	38·9	0·77
New rock gritstone ,, ..	69·7	0·67
Cannock Chase shale ,, ..	30·8	0·72
Pennant rock ,, ..	52·9	0·48
Cannock Chase siltstone ,, ..	49·4	0·43
Cannock Chase siltstone ,, ..	59·4	0·42

It will be seen that olivine, epidote, nepheline, muscovite, biotite, haematite, limonite, magnetite and ilmenite are practically completely decomposed by the treatment, whilst hornblende, augite, tourmaline and garnet are only partly decomposed, the quartz and felspar group being almost unaffected. The minerals which may possibly occur, therefore, in the residues from rational analyses of shales are quartz, the felspars, hornblende, augite, tourmaline, garnet, rutile, and barytes. Actually, in the course of the analysis of numerous samples of shales and coal-measure rocks from widely different areas, experience has shown that the residues contain little or no iron, which would indicate that hornblende, augite, tourmaline, and garnet do not occur to any appreciable extent in the residues. Assuming, however, that they do, consideration of the alumina-contents will show the maximum error likely to be introduced by the assumption that the residue consists of quartz and felspar only. Analyses of shales have shown that the residues rarely contain 0·1 grm. of alumina, ferric oxide, etc., and, assuming that this amount is the maximum likely to be encountered, the correction to the residue for "felspar" present would be approximately 11 per cent. If, however, in an extreme case the alumina, iron, etc., had actually been derived from tourmaline or anorthite (Al_2O_3, Fe_2O_3, approx. 40 per cent.), then, to obtain correct figures for the quartz present, the appropriate factor 2·5 must be employed, and the correction would then be roughly 5 per cent. Thus the error introduced by the assumption, that the residue consists of quartz and orthoclase, would in this case be approximately 6 per cent. In practice, the normal correction that has to be applied is of the order of 3 per cent., so that, even in the extreme case above, the possible error introduced by the correction is less than 2 per cent. In most cases it is undoubtedly much less, as is shown by the absence of iron from the residues. The above remarks apply only to analyses of coal-measure rocks and shales. When the rational analysis is applied to igneous rocks the correction is responsible for errors sometimes amounting to 20 per cent., so that absurd results are obtained.

TABLE IV

EFFECT OF "RATIONAL ANALYSIS" ON QUARTZ, FELSPAR, ETC.

Mineral	Decomposition		Analysis of mineral		Analysis of residue	
	Through 60-mesh on 100-mesh Per Cent.	Through 200-mesh Per Cent.	SiO_2 Per Cent.	Al_2O_3 Fe_2O_3 Per Cent.	SiO_2 Per Cent.	Al_2O_3 Fe_2O_3 Per Cent.
Quartz	1·2	5·8	97·31	0·90	98·53	0·78
Flint	3·2	7·2	—	—	—	—
Chalcedony	3·3	7·3	—	—	—	—
Opal	58·3	59·4	—	—	—	—
Orthoclase	3·4	7·7	64·04	20·83	65·51	19·79
Albite	1·0	5·1	66·90	21·58	67·27	21·12
Oligoclase	3·4	8·2	—	24·88	64·69	23·33
Olivine	98·2	94·3	40·21	11·18	58·83	14·47
Hornblende	21·3	35·0	46·64	25·70	51·47	23·25
Epidote	44·7	90·4	39·32	34·95	67·13	20·87
Nepheline	97·4	95·9	40·36	35·96	51·23	21·16
Muscovite	79·8	93·0	43·67	39·95	64·46	27·17
Biotite	—	98·1	38·54	44·75	71·43	20·53
Augite	—	57·4	41·66	22·43	50·03	11·60
Tourmaline	3·9	15·5	36·23	41·41	36·59	41·28
Kaolin	—	90·7	48·33	36·78	72·02	19·07
Haematite	99·9	99·9	—	—	—	—
Limonite	99·8	99·6	—	—	—	—
Magnetite	99·7	99·7	—	—	—	—
Ilmenite	99·8	99·6	—	—	—	—
Rutile	4·4	27·8	—	—	—	—
Barytes	3·4	29·4	—	—	—	—
Garnet	42·4	86·4	—	—	—	—
Sericite	64·4	63·8	59·24	26·56	94·51	3·58

The fourth source of error, *viz.* incomplete removal of the products of decomposition, tends to give high results. This has been found to be due almost entirely to the incomplete removal of the silica resulting from the decomposition of silicates present in the sample under analysis, and confirmation of this is afforded by the results given in Table IV. It will be observed that the silica-content of the treated mineral is invariably greater than that of the original material, the increase being greatest in cases where the mineral has been most affected by the treatment. The greatest increase is equivalent to 0·1 grm. of silica, which would, in the course of the ordinary analysis, produce a positive error of 2 per cent. It has since been found, however, that, by practically complete removal of the acid extracts during analysis, neutralisation with 50 per cent. sodium hydroxide solution, and washing the residues, if necessary, by decantation before neutralisation, the concentration of the Lunge solution can be kept constant, thus avoiding the dilution which neutralisation of excessive quantities of acid extract entails, with the consequent incomplete solution of the hydrated silica.

From the above experiments it would appear that the rational analysis for free silica, when applied to coal-measure rocks and shales, tends to give low results. With samples ground to 60-mesh I.M.M., mechanical loss and solution of quartz in alkali solution may reach a maximum of 1 per cent., and the correction applied to the residue may introduce an error of approximately 1½ per cent. in most cases, whilst incomplete removal of hydrated silica should not, with careful work, be responsible for errors larger than 1 per cent. As the first two errors are counteracted by the last, the probabilities are that the method can in general be relied upon to give results accurate within 2 per cent.

As a further test, Dr. Francis, of the Government Laboratory, and Mr. Clarence A. Seyler kindly collaborated in the analysis of samples by the rational analysis method. The results, which are given in Table V, show that agreement to 1 per cent. may be obtained by different analysts.

TABLE V

COMPARISON OF RESULTS OBTAINED FOR FREE SILICA BY DIFFERENT ANALYSTS

Sample	Analysts No. 1 Per Cent.	 No. 2 Per Cent.	 No. 3 Per Cent.	 No. 4 Per Cent.
1	—	Nil	0·5	—
2	5·9	8·0	7·5	—
3	19·1	19·4	20·4	—
4	28·7	—	30·8	—
5	48·8	42·5	43·1	—
6	28·2	25·2	26·0	—
7	21·9	19·3	20·7	—
8	61·0	58·8	59·0	—
9	72·5	70·4	71·2	—
10	Nil	Nil	Nil	—
11	38·6	38·2	37·7	37·7
12	36·4	35·6	38·0	38·0

ULTIMATE ANALYSIS.—Attempts have been, and, apparently, are being made at the present time, to calculate the free silica-content of a shale from its ultimate analysis. Although this analysis can be made with a high degree of accuracy, it is fallacious to assume that calculations based on the analysis must necessarily give accurate results. The widely divergent results that may be obtained by this method are shown in Table VI, where the free silica-content of several samples has been calculated, the minerals present being assumed to be, in the one case, quartz, felspars, kaolin, etc., and, in the other, quartz, micas and kaolin. Unless the chemist is supplied by the mineralogist with a list of minerals present in the rock, he has no definite facts on which to base his calculations, and with shales it is apparently extremely difficult to identify all the minerals present, even by microscopical examination.

TABLE VI

FREE SILICA-CONTENT OF COAL MEASURE ROCKS BY CALCULATION FROM ULTIMATE ANALYSIS

Sample	S.33	S.32	"Greys"	S.54	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
Silica	54·32	59·88	81·98	23·99	
Alumina	24·35	21·98	6·77	12·32	
Ferric oxide ..	4·27	4·62	6·33	31·18	
Lime	1·26	0·53	0·47	1·04	
Magnesia.. ..	0·69	1·60	0·36	2·43	
Potash	4·02	3·92	0·74	0·64	
Soda	0·73	0·66	1·90	0·01	
Loss on ignition ..	10·28	6·63	2·48	23·71	
Calculated free .. silica-content	11·4	19	64·2	4·0	Composition assumed to be quartz, felspars, kaolin, &c.
	17·6	34·8	67	11·5	Composition assumed to be quartz, micas, kaolin, &c.

Microscopical examinations of many of the coarse-grained rocks analysed by the rational analysis method have been carried out by Mr. S. H. Shaw, of the Geological Department, Birmingham University, and micrometric measurements have been made of the free silica. The results to hand at the moment show fair agreement with those of the rational analysis. It was hoped that a further check might be obtained by *X*-ray analysis of the samples, but information from the laboratories of Professor W. Bragg, of Manchester, is to the effect that results by this method have not a greater accuracy than ±5 per cent., so that no useful purpose would be achieved by having analyses made in this way.

It seems clear that, of the methods reviewed for the determination of free silica in coal-measure rocks, the method of rational analysis, when properly carried out, is by far the most reliable at the present time. Though the results obtained may be low by amounts up to 2 per cent., the method appears to be far more accurate than calculations from the ultimate analysis, micrometric measurements of shale sections, or *X*-ray analysis.

In conclusion, I wish to thank Mr. H. V. Thompson and Professor Sollas for their helpful suggestions, Dr. A. G. Francis, Mr. Clarence A. Seyler and Mr. S. H. Shaw for their kind co-operation, and Mr. J. Ivon Graham for his invaluable criticism and advice.

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[5] Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929. Hillebrand, *Analysis of Silicate and Carbonate Rocks*, U.S. Geol. Survey, Bull. 700.

Discussion

The PRESIDENT remarked that the Society was grateful to Mr. Shaw for the interesting paper on this question. He could realise the importance of the paper, especially if it had any bearing on the question of silicosis.

Dr. W. R. JONES thanked the President for the opportunity of contributing to the discussion of this interesting paper, which contained, in addition to the author's main conclusions, valuable data which had not been previously published. Table IV, for example, brought out very clearly the great variation, under identical chemical treatment, in the relative amounts of solubility of different species of minerals composed entirely of free silica, and also of different silicate minerals. He hoped that a study of that Table would prevent a repetition of such generalisation as made recently elsewhere, that free-silica minerals were more easily soluble in the lung than natural silicates. There were several minerals composed of free silica with widely varying degrees of solubility; there were dozens of natural silicates, also with very marked differences of solubility. The speaker did not think it was helpful, in the study of silicosis, to base far-reaching conclusions as to what happened in the lung, on such a sweeping generalisation, which had long been refuted by mineralogists.

He could not agree with the author's conclusion that the determination of the free-silicate content of coal-measure rocks by the method of rational analysis advocated in the paper, or by any other method of rational analysis, was more reliable than that obtained by complete chemical analysis followed by the allocation of the constituents to the actual minerals present in the rock. On the contrary, he believed, with other geologists, the reverse to be the case, and for this reason: the rational analysis was based on the erroneous assumption, as had been pointed out many years ago by geologists, that the alumina in many of these rocks could be allocated to potash felspar. Many coal-measure rocks, particularly those in the working-places in the anthracite collieries of South Wales (where 90 per cent. of all cases of silicosis in the British coal-mining industry occurred) contained no potash felspar at all; that mineral had been completely converted into sericite. Now the ratio of alumina to silica in sericite was as 1 is to 1·243, whereas in potash felspar this ratio was as 1 to 3·5; in other words, almost three times as much silica would be allocated to the alumina on the purely hypothetical and incorrect assumption that it was present as potash felspar, as would be the case when the silica was allocated to the alumina in the ratio for the mineral known to be abundantly present in these South Wales rocks.

Dr. Jones here showed on the screen a photomicrograph of a typical sandy shale from a colliery that was notable for the number of cases of silicosis contracted there. This sandy shale contained no potash felspar, but hundreds of fibres of sericite were clearly visible. He would ask how was it possible, with such a rock, to obtain the percentage of free silica by allocating the alumina, according to the rational analysis method, to potash felspar? He could understand the attraction of a method which would enable analysts to return the consistent results referred to in the paper, but would point out that the consistency was obtained by arbitrarily multiplying the alumina-content, in all these cases, by 5·41. With this type of rock the results would be consistently low in the free-silica content. Moreover, these rocks often contained one per cent. or over of titanium oxide, weighed as alumina by the rational analysis method, and this further contributed to lowering the percentage of free silica.

The unreliability of this arbitrary allocation of alumina could be seen in Table VI, where a difference of 17·2 per cent. (34·8 minus 17·6) was shown between the free-silica content of the first two samples. Yet the difference given in the potash content was only 0·1 (4·02 minus 3·92). Similarly, in the same Table, under S. 33, two arbitrary allocations of the same analysis showed a difference of 15·8 per cent. (34·8 minus 19) of free silica. He would ask the author if the figure 34·8 was not a misprint for 24·8, or thereabouts? He would like to put it on record that geologists in all countries, who had studied this question, had no faith in the results of rational analysis of certain types of rocks, such as many of the coal-measure rocks, and had frequently said so.

The speaker's criticism of parts of the paper did not, however, prevent him from congratulating the author on a valuable piece of research. The author had definitely shown that Lunge's method was unreliable, and had established that, by his modification of Selvig's method, it was possible, with rocks of certain types, to obtain the *relative* (not, the speaker submitted, the *actual*) percentages of free silica: that was a distinct advance on any other rational analysis method and would probably prove of economic importance in the pottery industry.

Dr. HALDANE remarked that Dr. Jones had referred to a statement of his (Dr. Haldane's) at a discussion of the Institution of Mining and Metallurgy, about the solubility of silica and other minerals. He thought Dr. Jones's statement was extremely misleading, but perhaps Mr. Shaw would deal with that later. In the Selvig method the stone being analysed was treated with strong acid again and again in order to decompose the silicates, so far as possible, but was not treated with strong alkali for two hours. The alkali was mainly sodium carbonate, and was used in weak solution in order to minimise the solution of pre-existing free silica present in the stone. Great precautions were taken not to dissolve any more of the free silica pre-existing in the rock than could be helped, and the figures given showed the amounts which were, nevertheless, dissolved in the not strongly alkaline solution. He was not going into the very vexed question of silicosis that evening, because it was a medical question, and he would not refer to it except to say that he disagreed very thoroughly and completely with Dr. Jones's conclusion on that point (not expressed at this meeting, but in another paper).

Dr. R. LESSING said that he thought that the difficulty about the so-called "rational" analysis was that the substances which one liked to isolate were destroyed in the course of this procedure, and that, he thought, was the main criticism which Dr. Jones had to make on the work put before the meeting. As one destroyed practically all the silicates, the only original material left over was free silica. Now, a true "rational" analysis would be something on the lines of the Sollas method. Apparently this method was not very accurate, and did not give good results. At the same time he would like the author to consider whether, by certain refinements which might be applied, the specific gravity separation in different solutions might be brought to such a pitch of perfection that the ideal of obtaining the original constituents of the sample in isolated form might be reached or approached. Then Dr. Jones and his brother geologists might be satisfied. On the other hand, he thought that it was quite clear that ultimate analysis to which certain arbitrary calculation was applied could not give them the results they would like to have.

From the point of view of silicosis, although that was not to be considered that evening, it might be interesting to know whether the method had been applied to silicotic lungs. One point in connection with Table IV had struck him rather forcibly, and it might, perhaps, furnish a bridge over the chasm between Prof. Haldane and Dr. Jones, on the question whether silicosis was caused by free silica or by other minerals such as sericite. Of all the materials examined in Table IV, it happened that sericite was the only one which left a residue containing 94 per cent., or something approaching the silica-content of pure quartz. That might be significant or not for its physiological effect. On the other hand, Dr. Jones had taken it for granted that only a small percentage of sericite was left as residue. He personally made it 35 to 37 per cent. Perhaps this might be worth very serious examination. It might be found that sericite, after all, would furnish a residue even without this drastic chemical treatment, which left the silica behind not differing greatly in composition from quartz, The investigation might be carried further in this direction. He differed from Dr. Jones, whose work he admired, in his criticism of the methods applied in this course of analysis. He appreciated his argument on the shortcomings of rational analysis from the point of view of the mineralogist. He thought, however, that the behaviour of the petrological entities under the chemical treatment applied to them might, on further study, give some indication of what was likely to happen, say, to quartz and sericite, when subjected to biochemical reactions in the lung tissue or the lymphatic juices.

Mr. E. M. **Hawkins**, speaking from the purely chemical side, said it had been his fortune (or misfortune) to have to do such analyses lately, and the Selvig method, as originally put forward, was a very long business, particularly where one had to work single-handed. He, therefore, thanked the author for speeding up the process. It should be remembered that, as a rule, the alumina found was from 0·3 to 0·9 per cent., so that with the factor 5·41 the amounts of felspar would be between 2 and 5 per cent. If this alumina should really be calculated to some other mineral than potash felspar and another factor should be used, the error in the "free silica" would not amount to more than 2 or 3 per cent. at the outside. He did not think that Dr. Jones's criticism was quite justifiable, for the purpose of these analyses was to show the difference between one shale and another. He thanked the author for this very interesting paper, and particularly for the way in which he had traced the various errors likely to occur, so that by the final method comparable results could be obtained.

Professor **Boswell** welcomed the account of methods of rational analysis described by Mr. Shaw, and expressed the hope that chemists would be able to develop them further, so as, if possible, to avoid the methods of calculation that had been criticised that evening. The amount of error introduced into the estimation of constituents other than free silica by multiplying by a theoretical factor depended, of course, on the quantity of silica in the rock. If the rock happened to be a high-silica material, the error would be small. The geologists' method of determining the mineral composition was to interpret the rational analysis by separation and examination under the microscope of the constituents. They recognised, however, that this was not an entirely satisfactory method, for while minerals could be separated from coarse-grained rocks, the technique became more and more difficult with fine-grained rocks, such as clays and shales. Although work was proceeding in this field, no technique was at present satisfactory. On the other hand, calculation of composition from chemical analysis was not a safe procedure. He (the speaker) therefore appealed for the extension of the methods of rational analysis, so as to avoid, if possible, the use of factors such as 5·41 for orthoclase felspar. In this connection he had had, during the war, to investigate the resources of potash in this country. Theoretically pure potash felspar should show 16·9 per cent. of potash, but if apparently pure samples yielded more than 10 per cent. of potash, they were exceptional. Thus the composition of even an individual mineral varied considerably from the theoretical figure given in the text-books.

Dr. B. S. **Evans** asked if the fuming with sulphuric acid in Mr. Shaw's process was essential; obviously it would tend to dehydrate the silica, thereby rendering it more difficult to dissolve in the alkaline solution afterwards employed.

Mr. J. I. **Graham** said that he would like to say a few words regarding the amount of time Mr. Shaw had put into this work. The subject seemed, perhaps, to be treated scantily in the paper, but he knew what a long time had been spent on the investigations and how carefully Mr. Shaw had gone into the various points. Another direction in which the rational-analysis method had been applied in the

Mining Research Laboratory was for the examination of the very small samples of dust which they were collecting from the air in mines. The analysis was done on 0·15 grm. instead of on 5 grms., as advised by Mr. Shaw, and the same procedure was followed, with the exception that they centrifuged before decanting. When they got down to the final residue, which they assumed was felspar plus free silica, they had recourse also to treatment with hydrofluoric acid. The total residue should have been alumina plus potassium sulphate, and a factor based on that assumption was used, *viz.* 2·01. The results agreed very well indeed with treatment as carried out by the method described by Mr. Shaw, in which the test was made on 5 grms. This work was done by Dr. Skinner, and he (Mr. Graham) felt that it supported the claim that the rational-analysis method, as advised by Mr. Shaw, was reasonably accurate. The quantity of felspar was only comparatively small and the error was not great. The error in any other known method for determining free silica was so great that it was worth while having a method like that of rational analysis, even if it were only correct within about 2 per cent.

Mr. SHAW, replying, said that Dr. Jones had referred to the action of alkalis on quartz and silicate minerals. It was a definite fact that quartz and other forms of free silica were more soluble than silicate minerals in alkaline solutions.

The work of Lunge, Schwartz and Doelter had shown that, whilst quartz was appreciably soluble in boiling sodium carbonate solution, it was necessary to digest the felspars with sodium carbonate solution under pressure at 200° C. for some weeks before they were attacked. Table IV showed the effect of acid treatment on various minerals. The extraction with Lunge solution was necessary to dissolve the hydrated silica resulting from the decomposition of the silicates by acids and had little or no effect on the silicates.

Referring to the question of calculations from the ultimate analysis, he wished to point out that the felspars had not been calculated from the alumina. He had followed the geological method of calculating the Norm, and had calculated the amounts of felspars, in the one case, and micas, in the second case, from the potash, soda and lime contents of the sample. Excess alumina had been assigned to kaolin and the remaining silica calculated as quartz.

He did not agree that it was erroneous to assume that the alumina in the residue from a rational analysis came from felspar. He had examined a number of samples from the anthracite district in South Wales, and the residues contained less than 1 per cent. of felspar. If, as Dr. Jones stated, these rocks contained sericite, then these analyses confirmed the fact that sericite was decomposed by the rational-analysis treatment, as he (the speaker) had thought from the results shown in Table IV. The high silica-content of the residue after treatment of the sericite by the rational analysis method was due, in his opinion, to the fact that the sample was not pure. It was extremely difficult to obtain pure specimens of many minerals, and if anyone could supply him with a sample of pure sericite he would be extremely grateful.

He disagreed with Dr. Jones's remarks concerning titanium oxide. Whilst titanium oxide was a common constituent of rocks, it was not present in amounts greater than 1 per cent. in the majority of cases. Moreover, ilmenite was completely decomposed by the rational-analysis treatment and rutile was partly decomposed, so that it was by no means obvious that the "1 per cent. or more of titanium oxide" would remain in the residue and be subsequently weighed as alumina.

The rational analysis, so far as he personally was concerned, was merely a means of determining the free-silica content of rocks and shales, and he was not interested in the amount of felspars or micas present, except in so far as it enabled him to apply a correction to the residue and so obtain a more accurate result for the free silica. He had used a modification of the rational analysis, introduced by

Mr. Graham and Dr. D. G. Skinner for the analysis of small samples, to estimate the free silica in the residue from a silicotic lung. Although duplicate analyses agreed well, he was not inclined to put too great faith in the method, as he thought that the result was considerably below what it should be, owing to solution of the fine quartz particles in the Lunge solution. Professor Sollas's method had been applied to English rocks with considerable success, but it did necessitate the presence of coarse-grained rocks. He had tried to improve the separation of fine-grained rocks by using a centrifuge, but had not met with much success. In any case, attempts to separate quartz from coal-measure rocks by this method were not likely to be successful, as there was always the possibility of the presence of soda-lime felspars in the rocks with specific gravities approximating closely to that of quartz.

He agreed with Professor Boswell's remarks concerning the calculation of the composition of a rock from the ultimate analysis. As a help to geological classification the method was, perhaps, useful, but his problem was to determine the actual amount of quartz present, and the geological Norm might have no relation at all to the actual mineral constituents of a rock.

With regard to the point raised by Dr. Evans, he agreed that excessive treatment with sulphuric acid might result in dehydration of the silica, with subsequent incomplete solution in Lunge solution. That was the object of controlling the temperature of the acid at 200° C. The idea of the method was to decompose all silicate minerals, necessitating strong attack with acid, and to remove the products of decomposition. He was of the opinion that fuming with sulphuric acid below 200° C. did not affect the solubility of the hydrated silica in alkali solution. The analyses of the residues of minerals (through 200-mesh) after treatment, given in Table IV, showed that a certain amount of silica remained undissolved, but the greatest amount was only equivalent to 0·1 grm. or 2 per cent. on the original sample.

Mr. Clarence Seyler wrote as follows:—The paper of Mr. A. Shaw is of great interest and importance, in view of the problem of the relation of silicosis to the amount of "free silica" in rocks. It confirms my opinion that the method of "rational analysis," as applied to argillaceous rocks, is the best available, if properly carried out with the precautions mentioned by Mr. Shaw. One of the most important points is the careful regulation of the temperature during the digestion with sulphuric acid. A thermometer should always be immersed in the liquid and the process carefully watched, so that the temperature does not exceed 200° C. Since adopting this precaution I have had no difficulty in getting reasonably consistent results. The objection that finely-divided quartz may pass into solution in the treatment with the alkaline solution is met by extracting the original material under the same conditions with the alkali and determining the dissolved silica. In my experience the amount so dissolved is small.

The only assumption involved in the method is that the "felspathic residue" has the composition of orthoclase, and can be calculated from the alumina. Since, however, the amount of alumina in the residue is nearly always small, the possible error from the assumption is also small. It can be minimised by making a complete analysis of the residue. No careful analyst would omit a petrographical examination of the specimen. In my experience the estimate of the quartz formed by experienced petrologists agrees remarkably well with the "rational analysis." It is a far simpler proposition to estimate the percentage of quartz from the ultimate analysis of the residue than from that of the original rock. The ferromagnesian minerals have been mostly removed, as well as the decomposable minerals which form the "argillaceous matter"; these are difficult to identify under the microscope and very variable in composition.

The determination of the amount of "free silica" (by which quartz is, no doubt, meant) has apparently lost some of its importance since the Silicosis Order has altered the definition of a "silica rock," which was formerly defined as one containing over 50 per cent. of quartz. In reality, however, I do not see how a "silica rock" can be defined without reference to the amount of quartz it contains. The classification of sedimentary rocks by geologists is in a very unsatisfactory condition. This had no great practical importance until the question of silicosis arose. I do not wish to offer an opinion upon what silicosis is and whether it is due to "free silica" or to silicates. As matters stand, however, it is very important to have working definitions of "silica rock," sandstone, grit (or "gritstone"), shale, and rocks of intermediate character. I do not think that such definitions should present insuperable difficulties. Sand and grit can be reasonably defined by the range of size of the particles. For most purposes only quartzose sand need be considered. To define a sandstone, not only the percentage of quartz and the size-range of the particles, but also the compactness of the rock would have to be considered. Loose sand is to the geologist a "rock," but it is not a stone. Probably the hardness could be used for purposes of differentiation, if a satisfactory measure of it were adopted. Rittinger's law, connecting the hardness with the work done in crushing, grinding or breaking and the new surface produced, would probably be useful, since the surface depends upon the fineness of the particles, especially those of the smallest size, which are the most dangerous. In any case, it appears to me that a siliceous sandstone must consist chiefly of quartzose particles, that is, as a dividing line must contain over 50 per cent. Thus the work of Mr. Shaw supplies us with a fair measure of at least one of the factors in the definition.

Mr. N. SIMPKIN sent the following contribution to the discussion:—
I have read the paper by Mr. A. Shaw with considerable interest, particularly in view of the fact that Mr. Graham of the Mining Research Laboratory at Birmingham was good enough some time ago to forward me full details of the method which Mr. Shaw has been using for the determination of free silica.

We have carried out a number of determinations of the free-silica content of various types of coal-measure strata from the Lancashire coalfield by the method which Mr. Shaw is using, and have found that in duplicate determinations very satisfactory agreement can be obtained; for example, with a rather highly siliceous shale duplicate tests yielded 43·26 and 43·89 per cent. of free silica, whilst another shale yielded 24·96 and 25·15 per cent. of free silica.

A further test of the method was made by comparing the results thus obtained with the results of the microscopical examination of certain coal-measure rocks. The latter determinations were made independently in the Palaeobotanical Laboratories of the Lancashire and Cheshire Coal Research Association, and the following table gives the results obtained with Mr. Shaw's method, as compared with micrometric measurements of the free silica. The latter method fails, however, when the grains of the rocks are of a certain fineness. With coarse and medium-grained rocks, however, it will be seen that very good results were obtained.

	Free Silica	
Material	Chemical Method	Microscopical Method
1. Siliceous shale	43·6	46·0
2. Mud stone	20·5	Grain-size too fine
3. Fine-grained shale	22·3	
4. Argillaceous sandstone	49·6	52
5. Sandstone	75·8	75·0

The agreement in the above table is good, particularly when it is realised that the determination by the chemical method was made on a piece of the material about half-an-inch thick cut out of a lump of the rock, the microscopical method being employed on the adjoining face from which this piece of rock was cut.

The Determination of Small Quantities of Germanium in the Presence of Arsenic

PART I

By S. A. COASE, B.Sc.

(*Read at the Meeting, May* 2, 1934)

It is known (Müller and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909) that germanium dioxide is reduced to monogermane, GeH_4, more readily in alkaline than in acid solution, but the electrolytic reduction in alkaline solution has not been attempted. Since arsenates are not ordinarily reduced in alkaline solution, the following investigation was carried out in order to develop a method for the rapid detection and determination of small quantities of germanium in the presence of large quantities of arsenic.

Germanium occurs widely, but in insignificant amounts (Petar, *Bureau Mines, Information Cir.*, 6401, for general information and list of minerals). Leaving out of account spectrographic methods, 0·1 mgrm. of the metal can be detected by precipitation as sulphide with hydrogen sulphide (Browning and Scott, *Chem. News*, 1917, **116**, 250), or by reducing a germanic salt to germanous oxide, using zinc and sulphuric acid (Bardet and Tchakirian, *Compt. rend.*, 1928, **186**, 637). Quantities of the order of 0·06 mgrm. of germanium have thus been detected in the Marsh type of apparatus (Müller and Smith, *vide supra*). Using sodium amalgam as the source of nascent hydrogen, they reduced germanium dioxide to monogermane, and, by thermal decomposition of the gas, obtained a mirror of metallic germanium in a combustion tube; this operation occupied 60 minutes. The detection in the presence of arsenic was not considered.

For the determination of germanium the following methods are available:

(i) Johnson and Dennis (*J. Amer. Chem. Soc.*, 1925, **47**, 790) precipitate germanium sulphide from 6 *N* sulphuric acid by means of hydrogen sulphide, and oxidise the sulphide with 3 per cent. hydrogen peroxide to the dioxide, in which form it is weighed.

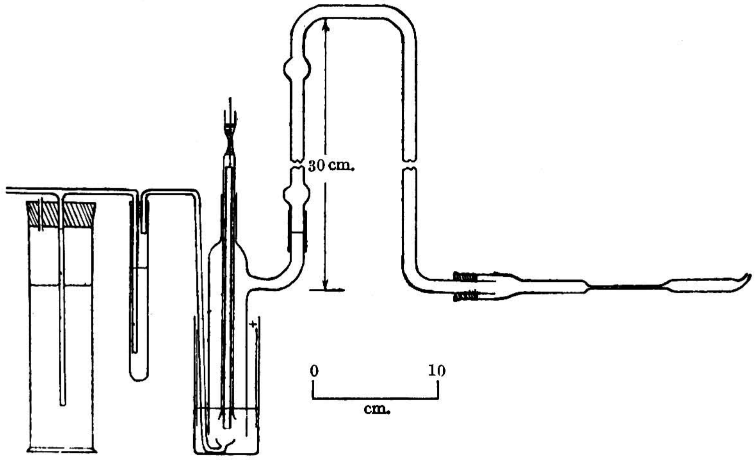
(ii) Müller (*J. Amer. Chem. Soc.*, 1922, **44**, 2493) adds to a solution of the dioxide a small excess of magnesium sulphate, and then ammonium sulphate, followed by ammonium hydroxide. The mixture is boiled for a few moments and allowed to settle for 10 to 12 hours, and the precipitate of magnesium orthogermanate, Mg_2GeO_4, is filtered off, washed, ignited, and weighed in this form.

(iii) Müller and Eisner (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 134) proposed the precipitation of germanium sulphide from 6 *N* sulphuric acid solution by means of hydrogen sulphide, and subsequent hydrolysis by means of boiling water to germanium dioxide. It may be noted here that Abrahams and

Müller (*J. Amer. Chem. Soc.*, **1932**, **54**, 86) claim quantitative separation of germanium and arsenic by using weak sulphuric acid (0·09 *N*), and passing hydrogen sulphide through the solution, when arsenic is precipitated (as a sulphide), but not germanium. Then the concentration of the acid is increased to 6 *N*, and the treatment is continued as described above.

(iv) Tchakirian (*Compt. rend.*, 1928, **187**, 229) has proposed two volumetric methods for the determination of germanic acid: *A*. In the presence of alcoholic compounds (mannitol, glucose, glycerol) the solubility of germanium dioxide is increased by the formation of germano-organic compounds. The liquid is titrated with sodium hydroxide solution, phenolphthalein being used as an indicator. *B*. A method based on the liberation, by mannitol-germanic acid, of iodine from a mixture of potassium iodide and potassium iodate. The reaction is complete in 12 hours, and the solution is then titrated with sodium thiosulphate solution.

New Method.—The method adopted in the present investigation was based on that described by Grant (Analyst, 1928, 53, 626) for the determination of antimony as stibine, but it was found necessary to replace the porous pot by a bell, since otherwise cataphoresis of the alkaline solution makes the method impracticable. The apparatus used is shown in the figure.



The cathode consists of a rod of nickel enclosed in a glass tube, flared at the end and provided with a small piece of rubber tubing which furnishes a suitable gas lock. From a tube, placed immediately under the cathode, hydrogen passes out. Monogermane formed is quickly carried away in the hydrogen stream to the combustion tube, where it is decomposed by heat. The hydrogen was obtained from a cylinder of the gas, passing through a safety trap and a bubbler. On test it gave a satisfactory blank. The anode is a sheet of nickel folded round against the side of the beaker. The current was obtained from the 200-volt mains with a suitable resistance. The voltage across the apparatus was 35 volts.

Procedure.—The procedure was as follows:—The solution to be electrolysed was placed in the beaker, the hydrogen stream turned on (two bubbles a second were found convenient, this speed being shown by the bubbler), and when the combustion tube, heated on the side of the constriction nearer the apparatus, had reached a dull red heat, the current was switched on. At the end of an experiment the current was first switched off and the passage of hydrogen allowed to continue until all monogermane formed in the cathode compartment had been swept into the combustion tube. The density of the metallic stain was matched against standards previously prepared.

The following conditions were examined to determine the best conditions of work:

(i) *Metal of the Cathode.*—Cadmium, stainless steel and lead gave no results. Magnesium, iron, copper and a specimen of stainless steel used in dentistry gave slight results, whilst nickel alone gave satisfactory results.

(ii) *Strength of Sodium Hydroxide Solution.*—It was found that the best yields were obtained with a dilute sodium hydroxide solution, but a limit is set by the necessity of maintaining a high conductivity. A solution of about 1·5 per cent. strength was used in the experiments described below.

(iii) *Current Density.*—It was found that a high current density favours a good yield of monogermane, but a limit is set by the need to prevent undue heating. With a higher current density it was found necessary to cool the beaker by a stream of water.

Artificial mingling of the anolyte and catholyte was tried. This was done by forcing the catholyte periodically into the anode chamber, the gas exit tube being closed for this purpose by means of a mercury seal. No appreciable effect on the yield of monogermane was, however, detected. When sodium nitrate or sulphate was added to the electrolyte the yield was unaffected. When sodium chloride was present the expected germanium deposit was obtained, but the anode was attacked and a precipitate formed in the beaker. A similar result was obtained in the presence of sodium nitrite, but this time the yield of monogermane was diminished.

DETECTION OF SMALL QUANTITIES OF GERMANIUM.—In these experiments 0·0273 grm. of germanium dioxide was dissolved in 3 ml. of 10 per cent. sodium hydroxide solution and 5 ml. of water. This was made up to 500 ml., and to aliquot parts 10 ml. of 10 per cent. sodium hydroxide were added, the volume being made up to 70 ml. by the addition of water. This solution was electrolysed in the apparatus described. In the last column are given the times for which electrolysis of the solution and heating of the combustion tube had to be continued in order to obtain a mirror of germanium. Results are given in the table below:

GeO_2 Mgrm.	Cathode area sq. cm.	Current amps.	Current density amps/sq.cm.	Time minutes
0·1092	1·4	5	3·5	15
0·0546	1·4	5	3·5	30
0·0273	1·4	5	3·5	45

In each case the germanium was readily detected by means of the mirror formed.

DETECTION IN THE PRESENCE OF ARSENIC.—Arsenic present in the electrolyte as an arsenate is not reduced, and the expected germanium stain is obtained.

Arsenic present as an arsenite must be oxidised as follows:—For every 0·2 grm. of arsenious oxide in 25 ml. of water add 25 ml. of concentrated nitric acid, and evaporate to dryness on a water-bath. The determination of germanium may then be made. As much as 340 mgrms. of arsenic calculated as As_2O_3 has been taken without interfering with the determination of the germanium.

THE DETERMINATION OF GERMANIUM.—Standard germanium mirrors were prepared by the electrolysis of solutions containing quantities of germanium, ranging from 0·0189 to 0·1 mgrm. These gave mirrors of increasing intensity in the combustion tube, and by comparison of the intensities of the metallic stains it was found possible to differentiate between quantities of germanium varying by 0·007 mgrm. The following additional standardisation was adopted:—Volume of solution to be electrolysed = 70 ml., made up of 10 ml. of 10 per cent. sodium hydroxide solution, germanium dioxide solution, and water to 70 ml. Area of cathode exposed to solution = 1·4 sq.cm. Current = 4 amps.

SUMMARY.—An electrolytic method for the determination of traces of germanium from 0·0189 mgrm. upwards in the presence of large quantities of arsenic has been described. The method is more sensitive than the chemical one of Müller and Smith. Experiments are being carried out at present on the latter method to investigate the possibility of its improvement, and, in particular, of its adaptability to the separation of germanium from arsenic.

I should like to take this opportunity of expressing my thanks to Dr. H. J. S. Sand, at whose suggestion this investigation was undertaken, for his interest and advice, and also to Dr. S. Judd Lewis for the germanium dioxide used in the experiments.

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

XXVI. The Interference of Tungsten in Earth-Acid Determinations

BY W. R. SCHOELLER, PH.D., AND C. JAHN

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

IN an earlier paper (VIII, ANALYST, 1927, **52**, 506), we have described new methods for the separation of tungsten from tantalum and niobium. The present Section deals with the position of tungsten in our proposed scheme of mineral analysis, based upon the conversion of the earth acids and their mineral associates into soluble organic complexes. We wished to ascertain whether tungsten, as a minor constituent of the minerals under discussion, could be quantitatively recovered with, or separated from, the earth acids through the application of our precipitation methods, and thus become a member of one of the analytical groups into which the constituents may be subdivided. We have previously shown that tungsten by itself is precipitated, though incompletely, by tartaric hydrolysis (XVI, ANALYST, 1929, **54**, 704), but is not precipitated from tartrate solution by tannin or cupferron (XVII, *id*, 710, 713).

With this end in view, we treated solutions of tantalum and niobium, containing known small amounts of tungsten, as described below, and examined the weighed pentoxide precipitates for tungsten (VIII, *loc. cit.*, p. 511), which was precipitated with tannin and cinchonine (VII, *id.*, 504). The determinations proceeded very smoothly, especially after introduction of a manipulative detail consisting in the thorough mixing of a cream of filter pulp with the suspension of the tungsten-tannin precipitate prior to the addition of cinchonine reagent. By adopting this simple expedient and omitting the boiling of the liquid after adding cinchonine solution, we entirely prevented formation of a gummy precipitate adhering to the beaker. After standing overnight, the liquid was decanted through a filter, and the pulp suspension was squeezed in the beaker with a glass rod for the removal of the solution; the suspension was then stirred up with cinchonine wash-liquor.

Before proceeding to describe our tests, we feel bound to refute Moser and Blaustein's misinterpretation (*Monatsh. Chem.*, 1929, **52**, 351) of our tannin cinchonine method. Two years after its publication these authors advanced a tannin procedure based on exactly the same principle as ours, namely, complete flocculation of the colloidal tungsten-tannin complex by means of an alkaloidal reagent; with this unessential difference, that they employ antipyrin instead of cinchonine. In introducing their method they comment upon ours to this effect (reference to our paper being omitted): Schoeller and Jahn had previously ascertained that tungstic acid is incompletely precipitated by tannin, but they succeeded in precipitating the balance with cinchonine, which had been previously advocated by Cremer. This reagent, which by itself precipitates tungstic acid, renders the use of tannin really (*eigentlich*) unnecessary.

We invite reference to Section VII (*loc. cit.*), which describes how the tannin cinchonine method was evolved, cinchonine alone having given us low results in presence of much alkali chloride. The reader will then be in a position to draw his own conclusion as to the accuracy of Moser and Blaustein's interpretation of our work.

EXPERIMENTAL PART.—The mixed oxides were fused with bisulphate, and the melt was dissolved in tartaric acid or ammonium oxalate solution, as specified below. Precipitation was effected:

(*a*) By hydrochloric acid from tartaric acid solution (tartaric hydrolysis), in Exps. 1 and 2 (XVI, ANALYST, *loc. cit.*, 704).

(*b*) By tannin from neutralised tartrate solution, in Exps. 3 to 7 (XVII, *loc. cit.*, 710).

(*c*) By tannin from faintly acid oxalate solution half-saturated with ammonium chloride, in Exps. 8 to 10 (XXIII, *id.*, 1932, **57**, 552).

(*d*) By fractional precipitation with tannin from oxalate solution for the separation of tantalum from niobium, in Exps. 11 and 12 (XXIV, *id.*, 1932, **57**, 751).

(*e*) By cupferron from tartaric acid solution, in Exps. 13 to 15 (XVII, *loc. cit.*, 713).

(*f*) By cupferron from oxalate solution, in Exps. 16 and 17 (as for (*e*)).

The precipitates thus obtained were ignited, weighed, and tested for tungstic oxide (*vide supra*), with the following results (in grms.):

	Taken				
Exp.	M_2O_5	WO_3	M_2O_5 ppt.	WO_3 in ppt.	Remarks
1	M_2O_5 0·1510	0·0148	0·1623	0·0127	$KHSO_4$, 3 grms.; $H_2\overline{T}$ 3 grms.
2	M_2O_5 0·1507	0·0150	0·1584	0·0107	,, 4 ,, ; ,, 6 ,,
3	none	0·0154	0·0012*	nil	* SiO_2 and Fe_2O_3.
4	Ta_2O_5 0·2050	0·0158	0·2066	0·0026	Used 1·5 grm. tannin.
5	Ta_2O_5 0·2006	0·0148	0·2098	0·0094	,, 2 grms. ,,
6	Nb_2O_5 0·2041	0·0150	0·2193	0·0124	,, 2 ,, ,,
7	Nb_2O_5 0·2047	0·0148	0·2168	0·0128	,, 2 ,, ,,
8	none	0·0158	*	0·0016	* Small ppt. after several days.
9	Ta_2O_5 0·2016	0·0152	0·2087	0·0078	Used 2 grms. tannin.
10	Nb_2O_5 0·2021	0·0150	0·2162	0·0132	,, 2 ,, ,,
11	Ta_2O_5 0·1546	0·0152	0·1538	0·0018	Ta fraction.
	Nb_2O_5 0·1547		0·1625	0·0065	Nb fraction.
12	Ta_2O_5 0·0528	0·0150	0·0582	0·0038	Ta fraction.
	Nb_2O_5 0·2023		—	—	Nb fraction lost.
13	Ta_2O_5 0·2000	0·0153	0·2111	0·0137	Ta_2O_5 recovery error: −0·0026
14	Ta_2O_5 0·2032	0·0150	0·2116	0·0118	,, ,, ,, : −0·0034
15	Nb_2O_5 0·2037	0·0158	0·2080	0·0049	Nb_2O_5 ,, ,, : −0·0006
16	Ta_2O_5 0·2018	0·0150	0·2122	0·0126	Ta_2O_5 ,, ,, : −0·0022
17	Nb_2O_5 0·2009	0·0158	0·2045	0·0041	Nb_2O_5 ,, ,, : −0·0005

CONCLUSIONS.—A glance at the Table shows that none of the procedures used achieves a complete precipitation of tungsten with the earth acids or its complete separation therefrom, but, instead, it distributes itself over the precipitates and filtrates. Hence, tungsten as a constituent of earth-acid minerals calls for a new procedure aiming at its complete separation from the earth acids, as well as from associated dioxide earths and other earths. With the help of our collaborator, Mr. A. R. Powell, we have succeeded in working out such a procedure by applying the principle of Bedford's method for the separation of tungsten from niobium, *viz.* the action of magnesia mixture on alkaline solutions of the metallic acids (ANALYST, 1927, **52**, 510). The process will be described in a forthcoming Section.

Several other conclusions and observations of analytical interest were obtained as the result of the above experiments:

(*a*) In tartaric hydrolysis, the earth acids induce precipitation of subordinate amounts of tungstic acid to a marked degree, though the tungsten precipitation is not quantitative.

(*b*) In all the tannin precipitation tests, niobium induces more pronounced tungsten precipitation than does tantalum.

(*c*) In Exp. 9 the co-precipitated tungsten discoloured the tantalum precipitate, to which it imparted a pale brown tinge. The same discoloration could not be observed in Exps. 4 and 5, since tantalum precipitates produced in neutralised tartrate solutions are invariably bleached by traces of co-precipitated iron (XIX, *id.*, 1931, **56**, 307, *D*).

(*d*) In the separation of tantalum from niobium a subordinate amount of tungsten, besides contaminating the earth-acid fractions, renders the fractionation less readily observed by reason of the slight brownish tinge of the tantalum precipitates; this may not appear at once, but only after a few minutes. The interference of tungsten is similar to, but less pronounced than, that of small amounts of titania (XI, *id.*, 1928, **53**, 264). It is more pronounced with low Ta:W ratios (Exp. 12); the filtrates may show a brownish-yellow tint.

(*e, f*) Like tannin, cupferron does not precipitate tungsten by itself, but partial precipitation is induced by the earth acids. We used 50 ml. of a 6 per cent. solution of the reagent in each test. The tantalum precipitates were crystalline in appearance; the niobium precipitates were plastic and adhesive, addition of filter pulp improving the filtration. In cupferron precipitations it is tantalum, not niobium, that induces more extensive tungsten precipitation; but the niobium recovery is more complete than that of tantalum, minute quantities of which were detected in the cupferron filtrates (XIX, *loc. cit.*, 310, *G*).

The above findings confirm an observation in Hillebrand and Lundell's *Applied Inorganic Analysis* (New York, 1929, 110, footnote) to the effect that, in separations by means of cupferron, "tungsten is partially precipitated no matter how much sulphuric and tartaric acids are used."

From what precedes, it appears to us that tungsten is the most troublesome minor constituent with which we have to deal in the analysis of earth-acid minerals.

SUMMARY.—When the earth acids are precipitated by tartaric hydrolysis, the co-precipitation of subordinate amounts of tungstic acid is incomplete. Neither tannin nor cupferron precipitates tungsten by itself from tartrate or oxalate solutions, but preponderating quantities of earth acid induce partial precipitation of tungsten. On account of its incomplete precipitation in all these procedures, we cannot yet assign to tungsten a definite position in our proposed analytical scheme. What we require is an additional method for the separation of tungsten from the earth acids as well as from other associated earths. A method to that end will shortly be published.

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ALDGATE, E.C.3

The Use of the Air-Damped Balance for the Determination of Total Solids in Milk

BY J. GOLDING, D.S.O., F.I.C.

(*Read at the Meeting, December* 6, 1933)

THIS paper should be regarded as only a preliminary communication, for, while the work was in progress with an air-damped balance of foreign manufacture, a new and even more sensitive air-damped, prismatic reflecting balance of British make has still further encouraged developments in the use of this type of balance for analytical operations.

Nevertheless, my experience with this new balance is limited to my own conditions, in which vibration is reduced to a minimum, and the extreme sensitiveness of the balance is an advantage. In my own case, my modifications in technique have removed difficulties and enabled me to meet requirements for a large number of determinations of total solids in milk, without increased laboratory accommodation or assistance for the work.

These difficulties have been overcome by the use of three new types of apparatus:—The first was an air-damped balance, which has greatly shortened the time and labour of weighing. The second was the use of small aluminium milk-bottle caps, which I adopted in place of large nickel dishes previously used, thus saving space and expense. The third was the adaptation of a syringe for measuring the milk before weighing—also a time-saving convenience.

The first air-damped balance used was a Kaiser and Siever balance, which has an illuminated scale on which a decigram and fractions of a decigram are shown; the open scale is divided into mgrms. The balance comes to rest in 15 to 20 seconds. The only weights required are the grams and decigrams, and this again saves time. Forty dishes containing total solids have been weighed on this balance, each to 0·2 mgrm., in 30 minutes. The tenths of a milligram are estimated, but the error should not exceed 0·0002 grm. at most.

I have recently obtained a still more sensitive air-damped prismatic reflecting balance by Oertling, having only one air-damping chamber. This has a very highly magnified, illuminated scale, graduated and marked up to 500 tenths of a milligram; no weights below 0·05 grm. are therefore used on the pan. With this balance it is possible to weigh to 0·05 mgrm. The balance, however, needs careful adjustment, and does not come to rest so quickly as the Kaiser and Siever balance. Thirty dishes containing total solids have been weighed on the Oertling balance to four places of decimals in 30 minutes.

Here 0·1 mgrm. is a reliable figure, but I do not attempt to use the fifth place of decimals, although the scale would admit of weighings to a greater accuracy than 0·1 mgrm. Both balances require a very firm support; I use brick piers specially built, but a wall bracket has served well with the Oertling balance.

The cost, a drawback to the air-damped balances, cannot be urged against the aluminium dishes or bottle caps, which are only 10s. 6d. per 1000. They are 44 mm. in diameter, 7·4 mm. deep, and 0·18 mm. thick, and vary in weight only from 1·1 to 1·3 grm. Before use the caps are rinsed with alcohol, followed by a fat solvent (Röse-Gottlieb distillates), to remove a trace of lubricant used in their manufacture; they lose only about 1 mgrm. by this treatment. They are easily cleaned and can be used again and again. They alter very little in weight if carefully cleaned and freed from traces of fat by means of alcohol and ether.

The great advantages of these small dishes are that they do not alter in weight while being weighed, and that they take up so small a space in ovens and desiccators. Our oven, which measures 14½ by 14¾ by 15½ inches, is fitted with five staggered copper trays. A supply of heated air is admitted at the four corners of the floor of the oven through four metal tubes. The intake of external cold air to these tubes is at the opposite side to that on which it is admitted into the oven. Each tube passes through the boiling water in the detachable water-bath under the oven, and the air is thus heated before it passes over the staggered trays. The oven door should fit tightly, and it is probable that the slightly higher results which were later obtained when milks were dried in front positions on the shelves, compared with those dried in back positions (see below), were due to a draught of cold air under our oven door. The oven will hold 245 dishes at one time.

Our technique for total solids consists in weighing the clean, dry dishes as taken from a desiccator, and, while they are still on the balance pan, introducing a syringe-full of well-mixed milk quickly into each dish, which is then weighed again. The syringe is adjusted to deliver just over 1 grm. of milk, which it does with great rapidity, and with a variation of not more than 3 mgrms. After delivering each sample it is quickly cleaned by rinsing it out with two or three fillings of milk. The weighed caps of milk are placed in rows on one of the copper trays, which is covered with a sheet of glass. When a batch of milks, up to 49, has been weighed out, the glass plate is removed and the tray is placed over a steam-bath for 15 minutes. After the milk has evaporated the tray is wiped underneath and slid into the oven.

After two to three hours, when the milks are dry, the dishes containing the solids are placed in desiccators holding 10 dishes each, cooled for 5 minutes, and weighed; a second weighing is taken after another hour in the oven. This reduces the handling of individual dishes to a minimum.

The results given in Table I indicate that the most concordant results are obtained after two to four hours' drying, and that further periods, even of 7 hours, in the oven give a slightly lower, but still closely agreeing, figure. Table I also shows the close agreement between 25 determinations made on the same bulk of milk, even though divided into four samples and weighed after different intervals in the oven.

Although a further loss of 0·001 to 0·05 per cent. may be obtained by further heating for 7 hours in the oven, the steady figure obtained after 2 to 4 hours is taken as correct. The old method of drying 5 grms. in a flat nickel dish, 3½ inches in diameter, gave slightly higher results.

For comparison, 44 pairs of determinations were carried out by the original method and by the new method with the Kaiser and Siever balance, side by side. The difference between the new and old methods worked out at —0·021 per cent., *i.e.* the old method gave a slightly higher result. The standard error of difference was ±0·0064.

The results available for a comparison of the methods are shown in Figs. 1, 2, and 3.

Figs. 2 and 3 are not strictly comparable with Fig. 1, as only 600 pairs of duplicate analyses have at present been made by the new method: 300 on each balance.

In each case the columns indicate the percentage of differences falling into the following groups:—

0=0—0·005 per cent., 0·01=·006 to ·015 per cent., 0·02=0·016 to 0·025 per cent., 0·03=0·026 to 0·035 per cent., and so on.

The average differences are given under each column, and also the number in each group per 100 duplicate determinations.*

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* If the percentage of total solids in the milk be regarded as the number of grms. of solids in 100 grms. of milk, then the unit of this figure may be regarded as grms. The expression percentage has been avoided in describing this and similar values because of possible ambiguity in its meaning.

Fig. 1 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 3461 samples of mixed milk from our typical herd tested between October 1st, 1928, and July, 1933. The figure indicates that small groups of differences tail out to a very unsatisfactory extent. The greatest difference between duplicates was 0·3 per cent., which was the difference between one pair of results in 3461 samples. About 98·5 per cent. of the samples

PER 100 DUPLICATE DETERMINATIONS

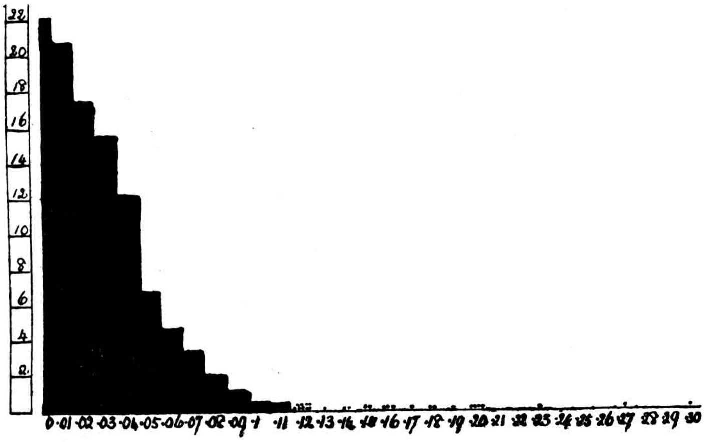

Fig 1. Old Method

Showing differences between duplicate determinations of the percentage of total solids in 3461 samples. Each dot (·) shows an error of the magnitude indicated in all the 3461 duplicate determinations

GROUP OF DIFFERENCES PER 100 DUPLICATE DETERMINATIONS

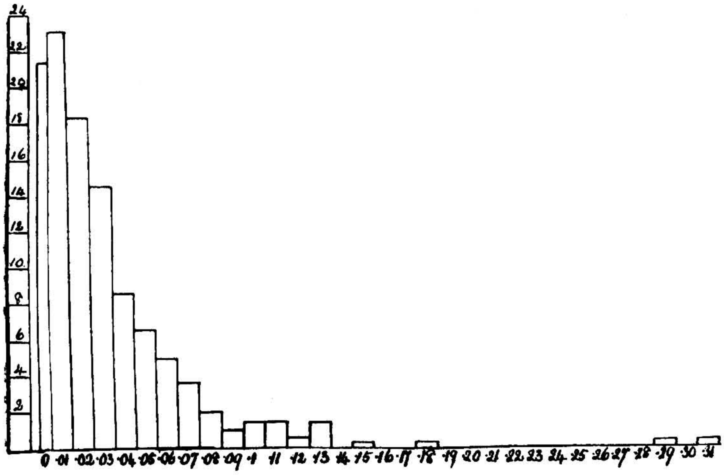

Fig. 2

Showing differences between duplicate determinations of the percentage of total solids in 300 samples. One grm. of milk used with air-damped balance weighing to 0·2 mgrm.

agreed within 0·1 per cent. of total solids, but the remainder were outside this range. Unfortunately, the cause of these occasional errors was not investigated at the time, but some tangible sources of error are indicated, and these provide another reason for revision of our old method. They were all made by the old method, in which about 5 grms. of milk was weighed into flat nickel dishes, 3½ inches in diameter,* and with the use of an ordinary analytical balance weighing to 1 mgrm. The standard difference is 0·04 grm., and the standard error of a single determination ±0·028 grm.

Fig. 2 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 300 samples of milk, about 1 grm. of milk being weighed in aluminium on the Kaiser and Siever balance, with an accuracy of 0·2 mgrm. The duplicate determinations were not made side by side, and were sometimes left until the following day. Even so, the standard difference is 0·05 grm., which makes the standard error of a single determination ±0·035 grm. In this case, although the speed was much greater, the accuracy is less than with the older and slower method.

Fig. 3 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 300 samples of milk, about 1 grm. of milk being weighed in aluminium dishes to 0·1 mgrm. on the new Oertling air-damped balance. The standard difference is 0·03 grm., and the standard error of a single determination ±0·021 grm.

The results show an improvement in accuracy over those given in Fig. 1 and Fig. 2.

As this method and technique give increased speed, improved accuracy, and economy of space and labour, they have been adopted.

In the work reported above, all the samples used were of fresh untreated milk. For such milk 1 grm. is the most convenient quantity to take.

In addition to those discussed above, nine series of 25 determinations each have been made on nine separate samples of milk. In each series the 25 dishes were distributed in 25 recorded positions in the ovens, with the object of finding out if the position in the oven contributed to slight differences of result which still persisted.

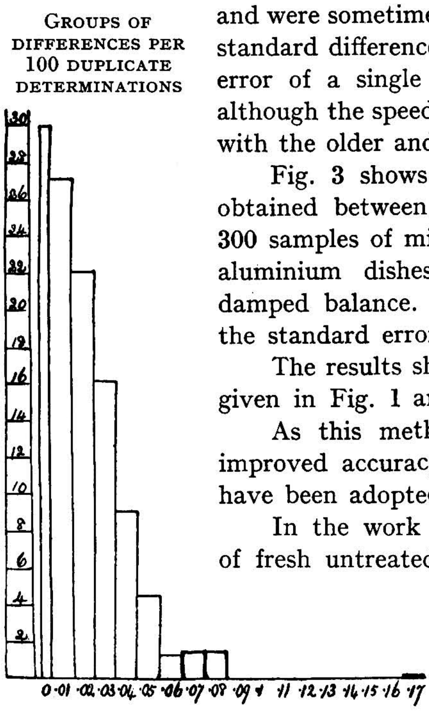

Fig. 3

Showing differences between duplicate determinations of total solids in 300 samples. One grm. of milk used with air-damped balance weighing to 0·1 mgrm.

All the results agreed well, and the differences were of the same order as those shown in Fig. 3. The standard error of a single determination was 0·022.

There appeared to be no significant difference between the different shelves. However, the samples dried in the front positions on the shelves showed a significantly higher value than those dried at the back of the shelves.

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* These can be obtained from Messrs. Alka, Ltd., Alka Works, Minerva Road, North Acton, N.W.10.

TABLE I

Total solids per cent. in four samples taken from one sample of mixed milk, showing the influence of the time of drying. Percentage calculated on each weighing of 1·015 to 1·0178 grms. of milk taken in 25 aluminium caps and weighed on an Oertling air-damped prismatic reflecting balance.*

Weighed at half-hour intervals and finally after 2 and 7 hours

Successive times in oven	Sample					Average
	I	II	III	IV	I	
½ hour	11·932	11·910	11·927	11·949	11·916	11·926
½ hour	11·892	11·880	11·897	11·910	11·887	11·893
½ hour	11·863	11·841	11·838	11·841	11·828	11·842
½ hour	11·843	11·821	11·848	11·861	11·828	11·840
½ hour	11·853	11·831	11·848	11·851	11·828	11·842
½ hour	11·843	11·841	11·838	11·831	11·828	11·836
2 hours	11·823	11·801	11·809	11·812	11·798	11·808
7 hours	11·813	11·801	11·819	11·812	11·789	11·806
	Weighed at 1-hour intervals					
	I	II	III	IV	II	
1 hour	11·931	11·899	11·920	11·880	11·904	11·906
1 hour	11·881	11·860	11·881	11·851	11·865	11·867
1 hour	11·871	11·830	11·861	11·831	11·845	11·847
1 hour	11·871	11·840	11·852	11·831	11·835	11·845
1 hour	11·841	11·820	11·842	11·812	11·835	11·830
1 hour	11·842	11·830	11·852	11·821	11·835	11·836
7 hours	11·832	11·820	11·842	11·802	11·826	11·824
	Weighed at 2-hour intervals					
	I	II	III	IV	III	
2 hours	11·837	11·855	11·843	11·822	11·856	11·842
2 hours	11·847	11·845	11·833	11·822	11·856	11·840
2 hours	11·847	11·835	11·813	11·832	11·837	11·832
7 hours	11·827	11·826	11·813	11·842	11·827	11·827
	Weighed at 3-hour intervals					
	I	II	III	IV	IV	
3 hours	11·869	11·865	11·848	11·847	11·830	11·851
3 hours	11·859	11·865	11·848	11·827	11·820	11·843
7 hours	11·839	11·856	11·839	11·827	11·820	11·836
	Weighed at 4-hour intervals					
	I	II	III	IV	I	
4 hours	11·868	11·863	11·854	11·835	11·841	11·852
4 hours	11·829	11·843	11·824	11·815	11·821	11·826
7 hours	11·809	11·843	11·844	11·835	11·831	11·832

* The third place of decimals is only an estimate; it is retained to indicate the nearest 1/10th milligram between successive weighings at intervals of time given in the margin.

The Roman numerals give the numbers allotted to the four sub-samples. The agreement between these indicates effective mixing.

The averages of 5 determinations after each successive period in the oven are given as percentages of total solids in the last column.

Of the deviations from the mean of all the determination, 76 per cent. of those which exceeded the mean by more than 0·015 per cent. were dried in front positions on the shelves.

By avoiding the use of the front positions on the shelves and packing the door of the oven, the standard error of a single determination may be reduced below 0·02.

With the object of avoiding frequent adjustments of the zero-point to obtain weighings of the total solids to 0·0001 grm., a second air-damping chamber is being added; this is expected to eliminate this difficulty.

In conclusion, my thanks are due to "Student," to Mr. L. McMullen and to Dr. S. Bartlett for statistical criticism, and to Mr. A. Wagstaff, who carried out most of the analyses.

THE NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING
SHINFIELD, NEAR READING

Vitamin *D* in Cacao Shell

BY ARTHUR W. KNAPP, M.SC., F.I.C., AND KATHARINE H. COWARD, D.SC.

CACAO seeds or "beans" consist of 87·3 per cent. of nibs (*i.e.* broken cotyledons), 0·7 per cent. of germ (radicle) and 12 per cent. of shell or husk (the spermoderm with adhering parts of pericarp and perisperm). The nib is the part used by the cocoa and chocolate manufacturer, and the shell is a by-product which is used in cattle food.

In 1928 milk chocolate of known composition was subjected by us to feeding tests for vitamin assay. The number of units of vitamin *D* found was greater than could be accounted for solely by the concentration of the milk, and, as the only other ingredients were sugar and cacao bean nib, it became evident that the cacao-bean nib must supply the remainder of the vitamin *D*.

As a result of this observation in 1928, we tested biologically a sample of nib prepared from Gold Coast cacao and confirmed the presence of vitamin *D*, the amount present being one unit of anti-rachitic activity per grm. of nib (see *J. Soc. Chem. Ind.*, 1932, 1008). The nib tested was free from shell, but contained the germ or radicle. Only a small amount of vitamin *A* was found, and no vitamin *B*. Other investigators have found vitamin *B*; Sasika and Wakayama (*J. Agr. Chem. Soc., Japan,* 1932, **8**, 160; C.A., 1932, **26**, 5326) have reported the presence of anti-neuritic vitamin *B* in cacao beans, and Labbé, de Balsac and Lerat (*Bull. Soc. Therap.*, 1931, 12, 36, 175; C.A., 1932, **26**, 2770) have found vitamin *B* in the cacao germ. The latter authors have also shown that cacao butter contains a small quantity of vitamin *A* (*Bull. Soc. Therap.*, 1930; *B.C.A.*, 1931, A, 988).

Our discovery of vitamin *D* in cacao nib caused us to consider how it had originated. We know that during the preparation of cacao beans for the market, that is during fermentation and subsequent drying, there is a passage outwards of various constituents of the nib (*e.g.* theobromine, tannin, and other substances at present unidentified into the shell (Knapp and Wadsworth, *J. Chem. Soc. Ind.*, 1924, 124T), and also, on the other hand, that the acids in the pulp on the outside of the shell pass inwards into the nib. The final constituents of the shell and nib are, therefore, closely interdependent. We know that both contain fat, and that the small quantity of fat in the shell is not markedly different from that in the nib. Our discovery of vitamin *D* in nibs led us to expect vitamin *D* in shell, and, since the seeds are exposed to the tropical sun for a number of days, it was reasonable to expect the shell to be appreciably richer than the nib in vitamin *D*.

Observations by Labbé, de Balsac, and Lerat (*Comp. rend.*, 1929, **189**, 864; *B.C.A.*, 1930, 121*A*) encouraged this expectation. They found in cacao two sterols, and these, particularly the α-theosterol, when treated with ultra-violet light, cured rickets. They noted that the shell was richer in these sterols than either germ or nib. They found 6 to 8 per cent. of sterols in the fat from the shell, as compared with 0·3 to 0·4 per cent. in the fat from the nibs.

For the purpose of testing for vitamin *D*, a sample of cacao shell was obtained in the factory from a full-sized commercial plant, so as to be representative of ordinary cacao shell. Shell from Gold Coast beans was selected for the test, as West Africa is responsible for more than half the world's cacao production. Most of the cacao produced on the Gold Coast undergoes fermentation. There is little or no artificial drying, the cacao being dried by turning over and over in the sun, a process which usually takes at least six days.

The beans were ordinary Gold Coast cacao, the grade known commercially as "good fermented" or Grade 1, and in this case actually contained about 98 per cent. of fermented beans and 2 per cent. of unfermented beans. The beans were passed through the cleaning plant and roasted, broken and winnowed in the ordinary way. The fraction consisting of large fragments of shell was taken. This contained only traces of nib or germ. The shell was ground to a fine powder to make it more suitable for feeding to rats.

The biological tests were carried out under the direction of one of us (K. H. C.) at the Pharmacological Laboratories of the Pharmaceutical Society. They consisted of an estimation of the vitamin-*D* content of the powdered cacao-bean shell in terms of the International Standard for vitamin *D*. The method of estimation was the one usual in those laboratories. Young rats weighing about 60 grms. were made rachitic by feeding them on a rickets-producing diet (Steenbock's 2965) for 3½ weeks. Half the rats of each litter used were given a single dose of irradiated ergosterol, the International Standard, at the beginning of the ten days' curative period, while the cacao-bean shell was given as a percentage of the diet of other rats throughout the ten days' curative period (in the first experiments) or as a small dose directly into the rat's mouth, 0·05 grm. on each of the first 5 days and none on the last 5 days of the curative period (second experiment). In the first experiment, the cacao-bean shell had been given as 1, 10 and 20 per cent. of the diet, respectively, one litter of rats being used to compare each of these quantities with a total dose of 5 units of vitamin *D*. Records of the amount of food eaten by each rat were made each day, and from these records the total amounts of cacao-bean shell eaten during the test were calculated.

At the end of the 10 days' curative period the rats were killed, the distal ends of the radii and ulnae were placed in 4 per cent. formaldehyde for a few days, then separated with a sharp scalpel, cut longitudinally, and stained by placing in 1·5 per cent. silver nitrate solution and exposing to sunlight. The calcified parts of the bones blackened, and it was thus possible to compare the healing produced in the different bones by the cacao-bean shell and by the standard vitamin *D*.

The healing in each bone was assessed by comparison with a series of bones showing graded amounts of healing given values 0 to 6. The ratio between the average amount of healing shown by a number of rats all given a certain dose of cacao-bean shell and that shown by other rats given a dose of the standard is not the ratio of the potencies of the doses. The ratio of healing is converted into the ratio of the potencies of the doses by finding the abscissae corresponding with these average amounts of healing from the curve of response relating healing to dose of vitamin *D* given.

The results of the first experiment with the cacao-bean shell may be seen in Table I.

TABLE I

Total dose	Litter	Rat	Healing
0·85 grm. C.S.	2742	5431	3·0
0·82 grm. C.S.		5432	4·0
5 units *D*.		5430	1·0
5 units *D*.		5433	2·0
9·5 grms. C.S.	2741	5426	6·0
7·9 grms. C.S.		5428	5·0
5·6 grms. C.S.		5429	6·0
5 units *D*.		5424	1·0
5 units *D*.		5425	1·5
5 units *D*.		5427	1·5
No dose	2744	5443	0
20·2 grms. C.S.		5440	6·0
19·4 grms. C.S.		5444	5·0
17·8 grms. C.S.		5446	5·0
5 units *D*.		5441	1·5
5 units *D*.		5442	2·0
5 units *D*.		5445	1·5

It was evident that the cacao-bean shell was much richer in vitamin *D* than had been anticipated. The first litter, *i.e.* the one on which the smallest amount of cacao-bean shell was tested, was the only one from which any calculation of the

TABLE II

Dose	Litter	Rat	Healing	Average Healing
No dose	2774	5599	0	0
0·25 grm. cacao-bean shell	2774	5598	2·5	2·4
		5603	3·0	
		5604	1·5	
	2775	5606	3·0	
		5608	2·0	
5 units *D*.	2774	5600	1·0	1·9
		5601	3·0	
		5602	2·0	
	2775	5605	2·0	
		5607	1·5	

CACAO-BEAN SHELL TESTS

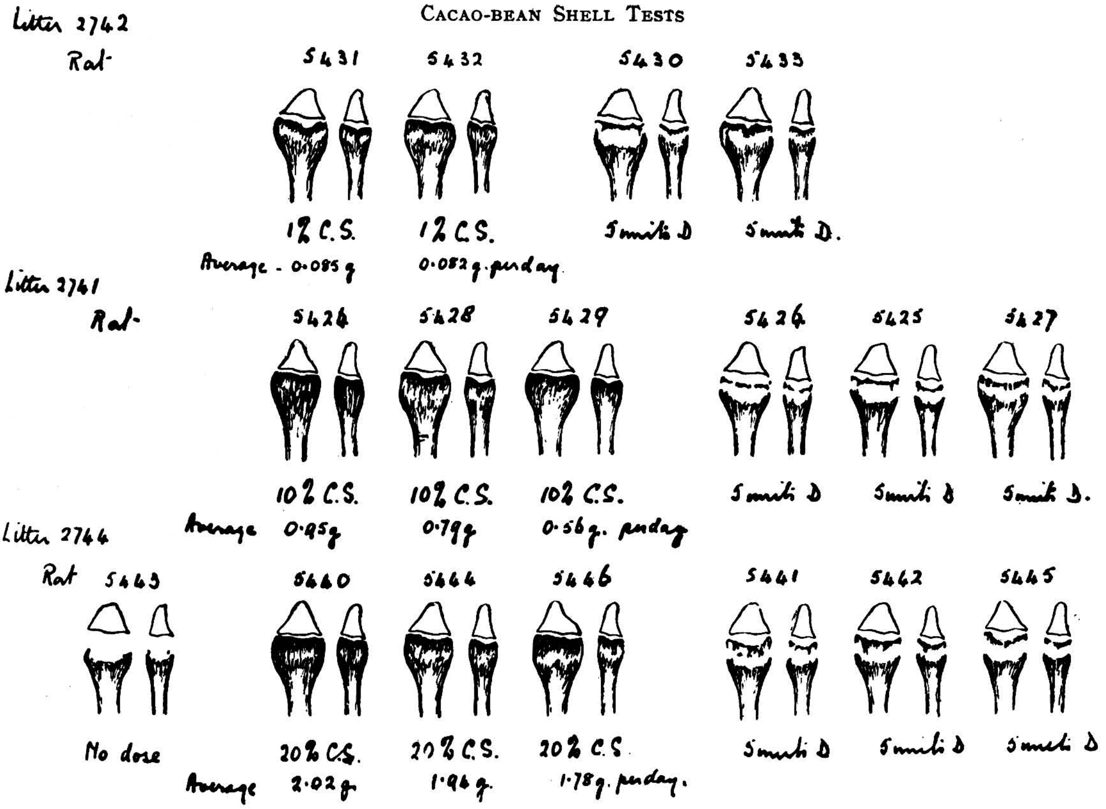

Fig. 1 (illustrating Table I)

The whole of the dose of Standard D was given on the first day of the test

CACAO-BEAN SHELL TESTS

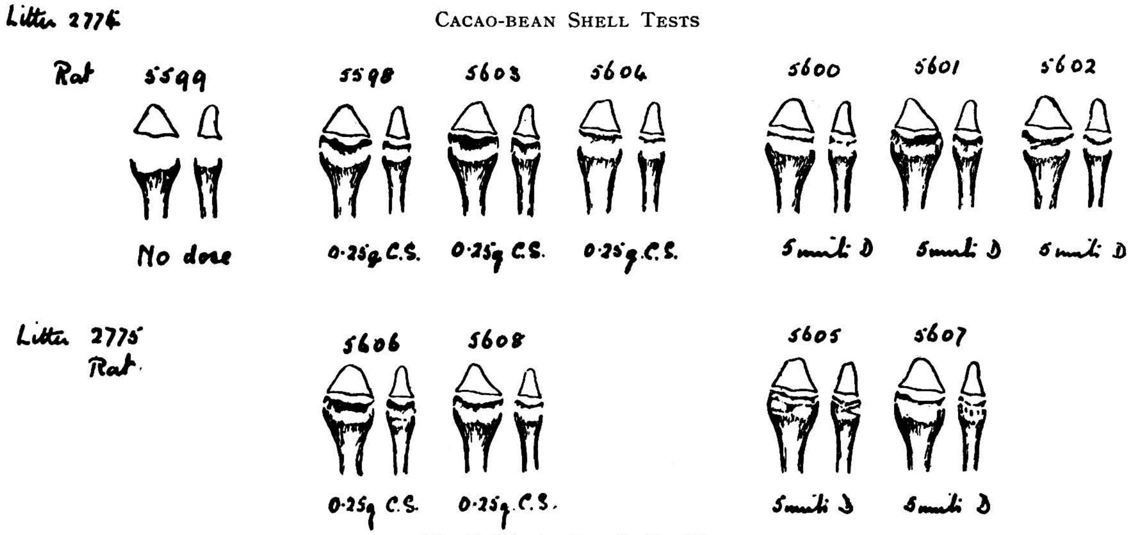

Fig. 2 (illustrating Table II)

Drawings of the calcified parts (only) of a radius and ulna from each rat used in the tests. A severe rachitic condition was produced in each rat as judged by the width of the metaphyses. The degree of healing produced by the cacao-bean shell was judged by the amount of calcification produced in the metaphyses of each rat.

potency could be made; in the other litters the healing brought about by the cacao-bean shell was too great for an accurate calculation. The first litter gave a value of 25 units of vitamin *D* per grm. of powdered cacao-bean shell, but, as only 4 rats had been used in this comparison, another test was made. A smaller dose of cacao-bean shell, 0·25 grm. altogether (5 doses of 0·05 grm.) was compared with 5 units of vitamin *D*. The result may be seen in Table II.

In this test the average healing of the rats given 0·25 grm. of cacao-bean shell was 2·4, and that of the rats given 5 units of vitamin *D* was 1·9. The abscissae corresponding with these averages of the curve of response relating average healing to dose of vitamin *D* were 0·18 and 0·13, respectively. Thus the vitamin *D* content of 0·25 grm. of cacao-bean shell is $\frac{0{\cdot}18}{0{\cdot}13} \times 5$ units $= 7$ units. Therefore, the vitamin *D* potency of the cacao-bean shell is estimated from this test as 28 units per grm. This result confirms the earlier ones, and it may safely be concluded that the sample of cacao-bean shell contains about 28 units of vitamin *D* per grm.

This potency in vitamin *D* is high for any product, and may be compared with a figure of 100 units per grm. which is given by an average sample of cod-liver oil. For a vegetable product the figure is quite exceptional. It raises the general question whether vitamin *D* is produced by exposure to the sun during the drying of other fat-containing products, *e.g.* copra, coffee, spice, oil-bearing seeds, nuts, etc. Dann (*Biochem. J.*, 1932, **26**, 151) has shown that native-produced palm oil has a potency of about 1/30th that of cod-liver oil, which is higher than that of plantation palm oils, presumably because it has been exposed to the tropical sun for long periods. One of us (K. H. C.) has already reported (*Lancet*, **1933**, **930**) the anti-rachitic activation of yeast by exposure to strong sunlight. It is worth noting that yeasts can always be found on the shells of fermented cacao-beans.

Manufacturers have often stated that they prefer sun-dried cacao to that dried artificially. One of the desirable changes in cacao beans is oxidation of the tannins, which takes place during sun-drying. In artificial drying, temperatures over 75° C. are liable to be reached, and this destroys the enzyme essential to oxidation. Not only does the sun's heat provide a suitable temperature but, according to recent work by Steinmann (*Z. Unters. Lebensm.*, 1933, **65**, 454), exposure to sunlight actually liberates cacao red which, in the presence of oxidase, is oxidised to cacao brown. A further possible advantage of sun-drying is that this may result in a higher vitamin *D* content in cacao shell, and possibly in nib.

The shell of the raw, fermented cacao bean contains 1 to 2 per cent. of a rather acid fat. During roasting a little of the cacao butter from the nib is absorbed by the shell, so that it is usual to find in the roasted cacao shell at least 3 per cent. of substances extractable with petroleum spirit. This extract is mainly fat, and if, as seems possible, the whole of the vitamin *D* is concentrated in it, it must have a very high potency.

SUMMARY.—A sample of shell from fermented sun-dried Gold Coast cacao was found to be rich in vitamin *D*. It contained 28 units of vitamin *D* per grm.

Notes

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

THE PREPARATION OF IODINE-FREE POTASSIUM HYDROXIDE

FOR the determination of the very minute quantities of iodine present in milk and other foods it is necessary to add relatively very large quantities of potassium hydroxide. This reagent, if of ordinary A.R. quality, frequently contains sufficient iodine to raise the value of the "blank" determination to a figure of the same order as that found in the actual analysis, and no very satisfactory method of purifying the reagent appears to have been placed on record.

A satisfactory electrolytic method of purification has been used for some time in the Government Laboratory, but this method is somewhat complicated, and it was realised that a simpler method would be welcomed by the various laboratories interested in work of this nature.

Von Fellenberg's method for the preparation of iodine-free potassium carbonate depends on the distribution of potassium iodide between a saturated solution of potassium carbonate and a solution of ethyl alcohol, the iodide being quantitatively extracted by the alcohol, but this method is not applicable to the purification of potassium hydroxide. Perusal of a recent paper by Gibby (*J. Chem. Soc.*, 1934, 9), on the system acetone—potassium hydroxide—water, indicated that an investigation of the distribution of minute quantities of potassium iodide between acetone and a saturated solution of potassium hydroxide might be of interest.

Accordingly, the removal of 4·0γ of added potassium iodide from a saturated aqueous solution of potassium hydroxide was examined, the aqueous solution being repeatedly extracted by shaking with an equal volume of acetone, and the acetone layers being examined separately for iodine. The results were as follows:

RECOVERY OF 4·0γ OF POTASSIUM IODIDE BY EXTRACTION WITH ACETONE

		γ
1st acetone layer contained		1·75
2nd ,, ,, ,,		1·27
3rd ,, ,, ,,		0·53
4th ,, ,, ,,		0·40
5th ,, ,, ,,		0·16
6th ,, ,, ,,	less than	0·1
Total		4·11γ

It appeared, therefore, that a new method of preparing iodine-free potassium hydroxide was available, provided that iodate, as well as iodide, could be dealt with in a satisfactory manner.

The method was finally tested by preparing a batch of iodine-free potassium hydroxide from a saturated solution to which had been added iodate and iodide in equal proportions, and in such quantities as to produce a "blank" of 2·0γ of iodine. A "blank" determination, carried out with this solution, after purification in the manner to be described, gave 0·12γ, indicating that the method of purification is efficient.

The details of the method are as follows:—The potassium hydroxide (125 grms.) is dissolved in sufficient distilled water to produce a saturated solution, and, after the addition of 0·25 grm. of hydrazine sulphate, the solution is boiled gently in a flask for about 30 minutes. After cooling, the solution is transferred to a separating funnel and extracted by shaking with an equal volume of iodine-free acetone (redistilled after addition of a little potassium hydroxide). The acetone layer is rejected, and the extraction with acetone is repeated 9 times (*i.e.* ten extractions in all, with acetone).

Finally, the aqueous solution of potassium hydroxide is boiled gently to remove traces of acetone, cooled, adjusted to 10 *N*, and, if necessary, filtered through a Whatman (No. 54) filter paper.

I wish to thank Sir Robert Robertson, the Government Chemist, for granting permission for the publication of this note.

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C. O. HARVEY

NOTE ON AN ATTEMPTED ADSORPTION INDICATOR METHOD FOR THE DETERMINATION OF ALKALI SALTS OF ORGANIC ACIDS

IT seemed desirable to investigate volumetric methods for the estimation of the alkali salts of organic acids by reactions involving the precipitation of less soluble salts. Although the search for a suitable adsorption indicator has not proved successful, the results obtained may be of interest.

The following dyestuffs have been tried as adsorption indicators for titrations, in neutral solution, of silver nitrate (*N*/5 and *N*/10) with sodium and potassium tartrate, sodium benzoate, and sodium salicylate, and for titrations, in neutral solution, of barium chloride (*M*/4) with sodium and potassium tartrate, and sodium citrate:—Afghan yellow, brilliant yellow, bromthymol blue, Chicago orange G, chloramine orange G, chlorazol fast orange AG, chlorazol fast orange R, chlorazol fast yellow, chlorophenine orange RR, chrysophenine, curucuphenine, di-iodo fluorescein, diphenyl fast yellow, eosin, fluorescein, malachite green, methyl red, phenol red, pyrazole orange R, rhodamine 6G, safranine, tartrazine, tetrabromo-tetrachlorofluorescein.

The following method of titration was adopted:—A measured volume of the silver nitrate or barium chloride solution was introduced into a glass-stoppered bottle, and the indicator was added, and then the solution of the organic salt in a quantity calculated to be slightly less than that required for complete precipitation. In another bottle a similar volume of silver nitrate or barium chloride solution was mixed with the indicator and a quantity of organic salt solution slightly greater than that required for complete precipitation. The solution in one bottle thus contained excess of barium or silver ions, whilst the solution in the other bottle contained excess of organic acid ions. The bottles were shaken to coagulate the precipitates, which were allowed to settle, and the bottles were then compared to ascertain if the precipitates or solutions showed any difference in colour. The results were confirmed by further titrations of mixtures in which the organic salt solution had been placed in the bottles first.

In general, it was found that any one dyestuff behaved similarly for all the titrations mentioned, the dyestuff being either adsorbed on to the precipitate under all conditions, or remaining always in the solution. An interesting generalisation was deduced, namely, that dyestuffs of the di-stilbene type are always adsorbed on to the precipitate, whilst the simpler mono-stilbene derivatives always remain in the solution. It will be seen from the list of dyestuffs given above, that attempts were made to find a dyestuff of an intermediate behaviour, but these attempts were not successful.

We are indebted to Messrs. The Clayton Aniline Co., Ltd., The Geigy Colour Co., Ltd., and Imperial Chemical Industries, Ltd., for gifts of some of the dyestuffs investigated.

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SOME BARIUM VALUES OF THE BUTTER-FATS OF DIFFERENT ANIMALS

THE accompanying table gives the barium-soluble and insoluble values of some butter-fats from different sources. The method employed was a volumetric one, involving the precipitation, in the cold, of the barium salts by a known volume of standard barium chloride solution, and titration of the excess of barium in the filtrate with standard potassium palmitate solution.

About 2 grms. of fat were saponified in the usual way and neutralised to phenolphthalein. The cooled solution was made up to 100 ml. with water, and 25 ml. (equivalent to 0·5 grm. of fat) were pipetted into a wide-necked 100-ml. flask to permit of vigorous shaking after bulking. The solution was diluted to about 70 ml. with distilled water, and 0·1 *N* barium chloride solution was run down the side into the flask, in amount equal to the titration value of the fatty acids in the flask, as calculated from the saponification determination.

Butter	Saponification value	Insoluble barium value	Soluble barium value	Volatile acids × $\frac{5\cdot6}{5}$	Difference (= soluble barium value minus volatile acids)
Goats' butter.. ..	—	180	—	31	—
	235	180	55	31	24
	229	179	50	31	19
Syrian samna ..	240	179	61	40	21
Hedjaz ,, ..	234	180	54	39	15
Iraq ,, ..	242	180	62	42	20
Sheeps' butter (Egyptian)	226	176	50	—	—
Cows' butter—					
Australian ..	229	181	48	36	12
	226	177	49	33	16
	228	181	47	33	15
Egyptian ..	229	181	48	33	16
	224	182	42	30	14
Gamoos' butter ..	226	180	46	36	10
	224	181	43	33	10
	226	176	50	36	14
	234	179	55	44	11
	234	178	56	43	13
	229	180	49	38	11
	232	181	51	38	13
	226	181	45	35	10
	226	180	46	37	9
	222	179	43	30	13
Indian "butter" ..	228	179	49	39	10
Coconut oil	259	213	46	—	—
Animal fat	196	190	6	—	—

The solution, before shaking, was made up to 100 ml., and then shaken vigorously for about 1 minute. Coagulation of the precipitate was rapid, except when the excess of barium over the insoluble acids was low, as with animal fat or vegetable oils. Under those conditions it was preferable to add a definite excess of barium, say about 5 ml., of 0·1 *N* solution more than the titration value of the acids.

The solution was filtered through a dry folded filter paper, the first 20 ml. or so being rejected, and 50 ml. of the clear filtrate were then transferred to an

Erlenmeyer flask and diluted with an equal quantity of water, and the barium was titrated with a 0·05 *N* solution of potassium palmitate in 85 per cent. alcohol, bromthymol blue being used as indicator.

The titration result (ml.) multiplied by 56 and divided by 5, gave the barium-soluble value in terms of mgrms. of potassium hydroxide per grm. of fat.

The method, which is simple and rapid, avoids the necessity of eliminating alcohol from the neutral soap solution or of washing the partly-soluble barium soaps with a fixed quantity of water, as in the Avé-Lallement process.

The results show that the barium-insoluble values are somewhat lower than those obtained by the Avé-Lallement method (reduced to the same units), but the difference between the values for normal butters and coconut oil or animal fat is approximately the same. Further, the barium-insoluble values of goats' butter or Syrian samna, in the few determinations made, are no higher than those of gamoos' butter; in fact, a fairly good agreement is revealed in the barium-insoluble values of butters from different sources.

When expressed in the same units (as mgrms. of KOH) the barium-insoluble values of butters, determined by the Avé-Lallement method (Bolton and Revis), lay between about 179 and 187, and the barium-soluble values between 40 and 50, whilst the barium-insoluble values of coconut oil and lard were, respectively, 219 and 189.

As was to be expected, the barium-soluble value increases roughly with the volatile acids of the Reichert–Meissl–Polenske process, and the difference between the two values, expressed in the same units, does not vary widely with butters of the same type. This difference in the accompanying table is seen to vary between the limits of 9 and 16 (as mgrms. of KOH per grm. of fat) for cows' and gamoos' butter, whilst the limits, as determined by the Avé-Lallement process, calculated from the results of Bolton and Revis for cows' butter, lay between 2·6 and 10·1.

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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 1933

OF the total number of samples (5635) examined, 5339 were submitted under the Food and Drugs (Adulteration) Act (including 76 appeal-to-cow samples), as compared with 5332 samples in 1932. One hundred and ninety-nine samples were reported to be adulterated.

ARROWROOT.—Between the years 1910 and 1932 inclusive, 1031 samples of arrowroot were examined, and, of these, 15 were found to be adulterated, 11 consisting of maranta starch, with varying quantities of foreign starch, whilst 2 consisted solely of a mixture of maize and potato starches, and 1 of sweet potato starch. The adulteration of arrowroot with sweet potato starch was first recorded by J. R. Stubbs (ANALYST, 1926, **51**, 400). More recently Stubbs found small quantities (about 1 to 2 per cent.) of a substance foreign to arrowroot, having some, but not all, of the characteristics of sweet potato starch. The matter was subsequently investigated by P. H. Jones, who found that "marble arrowroot" (*Myrosma cannifolia*) is occasionally mixed with arrowroot by the growers, under the impression that it is a species of maranta (*cf.* Abst., p. 493).

PEARL BARLEY.—During the years 1926 to 1932 thirteen of the 183 samples examined were faced either with talc (3 samples) or with maize starch (10 samples). The use of maize starch began in the year 1930, increased in amount during 1931, and has since decreased, possibly on account of the attention which has been drawn to the matter. It has been claimed that the use of a coating of talc is necessary to protect the grain from weevils, but Liverseege and Hawley (*J. Soc. Chem. Ind.*, 1915, **34**, 203) were unable to find any evidence of such protective action.

FAT IN CHEESE.—The following table gives the amounts of fat (calculated on the dry substance) in the samples of cheese examined between the years 1908 and 1932:

Type of cheese	No. of samples	Average Per Cent.	Extremes Per Cent.
American ..	20	52·1	29·2–58·1
Processed ..	17	50·7	45·7–54·9
Cheshire ..	121	50·3	41·1–57·5
Gorgonzola ..	14	49·7	41·0–55·5
Cheddar ..	9	49·6	45·9–53·2
Lancashire ..	98	45·4	42·3–57·1
Soft	12	33·3	2·8–56·1
Dutch	9		29·8–41·0

It is interesting to note that Lancashire cheese contained nearly the same average percentage of fat as Cheshire cheese, although often considered to be richer in fat.

WINE JELLY.—A sample, described on the carton as "Old English Wine Jelly," was found to contain 0·1 per cent. of absolute alcohol, equivalent to about 0·03 per cent. in the jelly prepared for table. The flavour and aroma of the jelly were apparently intended to imitate those of a wine jelly of port character. Wine of port character contains about 15 per cent. of alcohol by volume, so that the alcohol in the sample would correspond with not more than 0·2 per cent. of wine in the jelly prepared for table. The manufacturers have finally agreed to redraft their advertisements.

LEMONADE MIXTURE.—Three samples were returned as adulterated, owing to the absence of citric acid and the presence of tartaric acid.

RUM AND COFFEE.—A sample labelled "—— the original Rum and Coffee" contained 2·3 per cent. of rum and 30 per cent. of coffee extract, the remainder of the sample consisting of chicory extract and molasses. The sample was an informal one, and further action has not yet been taken.

LABELLING OF SAUSAGES.—A sample of sausages was found to contain 110 parts of sulphur dioxide per million. When this sample was purchased a notice was exhibited in the shop bearing the following words:—"All sausage sold in this shop contains preservative in accordance with the new Government Regulation." This is a misleading notice, since there is no Regulation which prescribes that sausages must contain preservative; in fact, they may contain preservative only under certain specified conditions.

Where a substance is labelled as containing preservative, the form of label is definitely fixed by the Regulations, and it is further required that:—"No comment on or explanation of the prescribed declaration (other than any direction as to use in the case of a preservative) shall be placed on the label or on the wrapper or container." Apparently no such requirement has been authorised in the case of a notice in a shop and so the misleading form mentioned above cannot, for the moment, be regarded as illegal.

SULPHUR TABLETS.—A sample, submitted as sulphur tablets, was labelled "Lime-juice and sulphur." The tablets were coloured by means of an artificial dye to a pale shade of that yellow-green colour which would appear to be traditionally attributed to lime juice. The tablets were devoid of lime juice, but were flavoured in imitation of essential oil of limes. The vendor has been cautioned.

INDIGO AND TALC IN SWEETS.—An informal sample of boiled sweets was of the praline type, having very dark centres. On examination they were found to contain 0·7 per cent. of some colour having the characteristics of indigo. This is an unusually large amount. Indigo is not one of the prohibited dyestuffs, but the use of such a large amount of any colouring matter does not appear to be desirable.

Another sample of boiled sweets was found to contain about 0·2 per cent. of talc or French chalk. The presence of talc is undesirable, and, as most manufacturers do not use it, apparently unnecessary. Its presence probably arises from the fact that it is used to line the moulds in which the sweets are allowed to set.

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.

INSUFFICIENCY OF WARRANTY

ON May 18th a firm of grocers was summoned at Marylebone Police Court, by the Hampstead Borough Council, for having sold pearl barley which contained 1·2 per cent. of talc and 190 parts per million of sulphur dioxide.

Mr. F. C. Forward, for the Council, said that the barley was bought at a cheap price, and that the presence of talc must have been apparent.

Dr. Cox, Public Analyst for Hampstead, said that the large amount of talc on this barley was very evident, and any grocer could have seen that it was present. He agreed, however, that amounts of talc up to 0·5 per cent. were tolerated on barley and rice, but no sulphur dioxide was allowed in barley.

The defence was a warranty, and evidence was called to prove that those who handled the barley had no reason to believe that it was anything but what the warranty stated. The buyer said that there was nothing about the barley to suggest to him that it was adulterated. It was barley of medium quality costing 8s. 3d. per cwt.

The Magistrate (Mr. Ivan Snell) said that he thought that the buyer had not taken sufficient care, and that the warranty therefore failed. The defendants were fined £2, with three guineas costs.

SALE OF SO-CALLED "DUTCH CHESHIRE" CHEESE AS CHESHIRE CHEESE

On May 10th, 1934, a firm of provision merchants was summoned at Kingston upon Hull Police Court for selling, to the prejudice of the purchaser, 1 lb. of Cheshire cheese which was not of the quality demanded by the said purchaser, inasmuch as it was deficient in fat to the extent of 11 per cent.

Mr. J. E. Fishwick, for the Hull Corporation, said that this was one of those cases in which there was no statutory standard, and that the Stipendiary Magistrate must fix one for himself upon the evidence called before him (*Roberts* v. *Leeming*, 69 J.P., 417; *Wilson and McFee* v. *Wilson*, 68 J.P., 177; *Preston* v. *Jackson*, 1929, S.J., 712). The Corporation contended that the standard for Cheshire cheese was at least 45 per cent. of fat calculated on the water-free substance; evidence would show that the standard of the commercial product was nearer 50 per cent. of fat, but even if his Worship found the standard to be less than 45 per cent., an offence had been committed if he found the standard to be more than 34 per cent. Furthermore, Cheshire cheese was a whole-meat cheese. The sample supplied was found to be deficient in fat to the extent of 11 per cent. (or 25 per cent. calculated on the fat), assuming the standard for fat to be 45 per cent. on the water-free substance.

It was further stated that there was a notice, "Dutch Cheshire" on the cheese. The agent had neither seen nor been able to see the notice until after the purchase. In any case, he would not understand the term "Dutch Cheshire Cheese." A notice, to be a good defence, (*a*) must be either seen by or brought to the notice of the purchaser, and (*b*) the purchaser must understand it. (*Hayes* v. *Rule and Law* (1902), 87 L.T. 133; *Collett* v. *Walker* (1895), 59 J.P. 600; *Star Tea Co.* v. *Neale* (1909), 73 J.P. 511; *Redbourne* v. *Hudson* (1925), 89 J.P. 25).

The Stipendiary Magistrate observed that what the prosecution were really saying was that Cheshire cheese was asked for and that when the sample was analysed it was found to be deficient as Cheshire cheese. Mr. Fishwick agreed.

Evidence was given of the purchase of "1 lb. of Cheshire cheese," for which 8d. was paid. The inspector was subsequently informed that the cheese was not English Cheshire cheese, but was "Dutch Cheshire" cheese. On leaving the shop the witness noticed on the display counter a label marked "Dutch Cheshire." He had not noticed it previously, and could not have seen it from where he was served.

Mr. A. R. Tankard, F.I.C., the Hull City Analyst, said that the sample was not Cheshire cheese. Cheshire cheese was a whole-meat cheese, *i.e.* one made from substantially whole milk. The sample contained 16·3 per cent. of fat, whilst Cheshire cheese would have contained 24 per cent. or more of fat. Calculated on the dry substance, the fat in the cheese was 34 per cent., whilst in a whole-meat cheese the minimum should be 45 per cent. on the dry substance. He had never met with Cheshire cheese containing less than 45 per cent. of fat.

Of 132 cheese samples passing through his hands, 49 were sold as Cheshire cheese, 35 being purchased prior to this year, the minimum fat-content being 47 per cent. on the dry matter. The maximum was 60 and the average 52. Of the 12 samples bought this year since the sample at issue, the fat average was 51·2 per cent. on the dry matter; the lowest figure was 46·8, and the highest 57·6, so that the average amount of fat in Cheshire cheese, as now sold in Hull, was 51·2 per cent. It not only complied with the standard set up (45 per cent. fat on the dry matter), but more than complied with it. The sample in question was a skimmed-milk cheese. Cheshire cheese was known to him as a whole-meat cheese, because (i) of the method of manufacture; (ii) his experience as a Public Analyst confirmed that it was a whole-meat cheese; (iii) the published authorities so described it; and (iv) the Government had accepted this standard of 45 per cent. fat as a general requirement in connection with the grading of Cheshire cheese.

The witness quoted authoritative publications showing that Cheshire cheese was made from substantially whole milk, and he stated that as a whole-meat cheese it contained a ratio of fat to protein which was characteristic. The fat usually exceeded the protein in amount, and the ratio of fat to protein varied from 1·0 to 1·5 : 1. On the other hand, the amount of protein exceeded the fat in skimmed-milk cheese, and this ratio was then less than 1·0 : 1. The present sample had a fat : protein ratio of 0·63 : 1.

Mr. Tankard went on to show that 1000 lbs. of milk (97 gallons) would yield from 94 to 100 lbs. of cheese, according to fat-content and other factors. He calculated that milk containing the minimum of 3·0 per cent. fat would yield a cheese containing at least 46 to 51 per cent. of fat according to the probable amount of moisture present, and 52 to 58 per cent. of fat if the yield of cheese was less than 10 per cent. of the weight of milk used. In further proof of his statement that this cheese was a skimmed-milk cheese, and therefore not a Cheshire cheese, he calculated, by a well-known formula, that from its composition it was made from milk containing not more than 2·0 per cent. of fat. The deficiency in fat of this cheese meant a loss in energy-value as compared with a whole-meat cheese, which had 100 points of food value (expressed as calories) compared with 66 points for the skimmed-milk cheese sold to the sampling officer. The witness expressed his firm opinion that this sample of cheese could not be described as "Cheshire cheese"—it was not Cheshire cheese.

In cross-examination the witness agreed that the Ministry of Agriculture had not fixed a standard for fat in cheese. He did not agree with the suggestions made by Mr. Pearlman that the real reason why no fat-standard had been fixed was that there was a demand for cheap cheese of Dutch type which the country was not producing adequately, or that in Cheshire, in order to meet this demand, there was a great variation in the percentage of fat in Cheshire cheese.

Mr. S. Ernest Melling, F.I.C., Public Analyst for the County of Cheshire, etc., said that he had analysed a portion of the sample of cheese in this case, and found 16·2 per cent. of fat. He agreed substantially with Mr. Tankard's opinion on this sample as expressed in his certificate. On the 45 per cent. fat-standard, the fat was deficient to the extent of 22 per cent. Mr. Melling said that his analyses of nearly 1000 samples of cheese submitted as "Cheshire cheese" showed it to be a whole-meat cheese containing from 46·4 to 61·4 per cent. of fat on the dry solids. He had not come across a Cheshire cheese deficient in fat for several years. He had made investigations into the composition of Cheshire cheese produced strictly by the usual methods, and had found that, following the process throughout, a milk containing 3·44 per cent. of fat and 8·80 per cent. of non-fatty solids yielded about 10 per cent. by weight of cheese containing 36·0 per cent. of moisture, 33·65 per cent. of fat, and, on the dry matter, 52·6 per cent. of fat. Similarly, when the milk used contained 2·71 per cent. fat, the cheese showed 43·7 per cent. of water, with 24·9 per cent. of fat or 44·1 per cent. of fat on the dry matter. It would appear quite certain that the sample of cheese in question here was derived from milk containing about 2 per cent. of fat. Such a cheese was not entitled to be called "Cheshire cheese," which, in food-value, was 50 per cent. superior. He did not recognise, he said in cross-examination, "Dutch Cheshire cheese," which was a misnomer.

Mr. W. B. Mercer, B.Sc.(Agric.), Principal of the Cheshire School of Agriculture, also gave evidence. Cheshire cheese, he said, was universally regarded in his area as a whole-meat cheese, and he accepted the definition of whole-meat cheese which had been given. The method of manufacture of this cheese involved the use of whole milk, and the product invariably contained over 45 per cent. of fat on the dry matter. The average fat in Cheshire cheese was found by him in

1928 to be 49 per cent. on the dry sample, and similar figures could be quoted for later years (an average of 51·9 per cent. of fat on 68 recent samples). The Cheshire Cheese Federation had adopted the standard of 45 per cent. on the dry matter of the cheese as a guaranteed minimum.

Mr. Pearlman, for the defence, emphasised the point that the notice was conspicuously displayed on the cheese, and it should have prompted the purchaser to inquire what he was getting. He did not demand any quality, but asked for Cheshire cheese and received Dutch Cheshire cheese.

The Stipendiary Magistrate, announcing his decision, said that he thought it should be made absolutely clear that this was not a case of passing off foreign produce as British produce and describing it as such. When people went into a shop, he continued, they were entitled to get what they asked for, or to be told that the shop did not sell it. He found that the purchaser in this case did not see the notice referred to. With regard to Mr. Pearlman's second point, that Dutch Cheshire cheese was Cheshire cheese, the Stipendiary Magistrate accepted the evidence of the Corporation's witnesses as to what had to be found in Cheshire cheese before it could be so called. He had no difficulty in saying that the cheese concerned in this case was not Cheshire cheese, and was therefore not the cheese for which the Corporation's representative had asked. Imposing the maximum penalty with £15 15s. costs, Mr. Macdonald said that he thought people of the standing of the defendants—who were not small shopkeepers—were people who could have afforded to take expert advice on such a point before starting to sell the article under any description.

Department of Scientific and Industrial Research

THE INDUSTRIAL APPLICATION OF X-RAY CRYSTAL ANALYSIS*

In this pamphlet of 15 pages an explanation is given, with photographic illustrations, of the ways in which X-rays are now used to determine the structure and condition of materials used in industry.

The Introduction describes briefly the principles of the method, and shows how the nature of the pattern produced by the diffracted rays, and recorded on a photographic plate, depends not only on the chemical structure of the material, but also on other factors, such as the size of the crystal grains, the distribution in direction of these grains, and the approximation to perfection attained by the crystals during their growth.

The information to be derived from the X-ray pattern is summarised under the following heads:

THE GENERAL NATURE OF THE MATERIAL.—Single crystals and crystal aggregates give different types of pattern, the former consisting of isolated spots, and the latter of a series of continuous lines. Problems concerned with single crystals seldom arise in practice; one example is the determination of the orientation of synthetic jewels used as pivot bearings. The wear and friction depend on the nature of the crystal plane on which the pivot rotates, and this plane can readily be determined by an X-ray examination.

THE SIZE OF THE CRYSTAL GRAINS.—The nature of the pattern varies with the grain size, and has one of three forms according to the size. When the linear

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* London: Issued by the Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W., May 28th, 1934. Enquiries concerning the facilities of the National Physical Laboratory for carrying out investigations on X-ray crystal analysis should be addressed to the Director, the National Physical Laboratory, Teddington, Middlesex.

size is much less than 10^{-5} cm. the lines lose their sharpness, and the size of the crystals can be measured by measuring the increase in the breadth of the lines. Measurement of crystal grain size is of great importance in such questions as the spreading power of paints, the activity of catalysts, and the physical properties of electro-deposited metals and metals in general.

THE ORIENTATION OF THE CRYSTALS IN AN AGGREGATE.—The crystals of an aggregate may be distributed entirely at random, or may show a more or less pronounced tendency to take up some particular orientation. This occurs frequently as a result of cold-work processes, such as the rolling and drawing of metals, and is also characteristic of many fibrous substances. Successful applications of the method have been made in the study of metals (in which the presence of fibre structure is of great importance), textile fibres, rubber, etc.

THE STATE OF PERFECTION OF THE CRYSTALS.—The presence of internal strain results in a distortion of the crystal cells, and this distortion shows itself in the X-ray pattern by a loss of sharpness of the diffraction lines. If the breadth of the lines is measured, a measure of the degree of strain is obtained. The method is not confined to the study of metals or the detection of strains in castings, welds and the like, but is also applicable to other substances such as natural graphite, the physical properties of which vary with the degree of imperfection of the graphite crystals formed from the amorphous carbon.

THE CHEMICAL NATURE OF THE MATERIAL.—Each chemical compound (not merely each chemical element) has its characteristic atomic arrangement, and its own characteristic X-ray diffraction pattern by which it can be identified. An approximate analysis is usually practicable, although exact quantitative analysis by means of X-rays presents considerable difficulties. Moreover, the method fails to take account of amorphous material. An example of the application of X-rays to chemical problems is afforded by the determination of the composition of thin scales on steel boiler tubes which had burst under puzzling conditions. Without removing the scale, the particular oxides of iron forming it were identified not only at different points on its surface, but also at different depths.

Other chemical applications consist in the detection of impurities, the study of solid solutions and mixtures, and the examination of allotropic modifications. For example, by the use of X-rays it is possible to determine immediately whether a specimen of silicon dioxide is α- or β-quartz, cristobalite or tridymite.

CHANGES IN STRUCTURE PRODUCED BY PHYSICAL TREATMENT.—A typical example of this application of the method is its use in the examination of magnet steel before and after heat-treatment in manufacture. It is shown how an internal strain, which is apparently desirable in such steel, disappears if the steel is heat-treated at 900° C., but reappears when it is heat-treated at 1200° C. On the other hand, experiments on two electrical transformer steels show how the magnetic losses of such steels are reduced as the crystals are rendered free from strain, as indicated by the X-ray photographs.

Ministry of Health

ANTIMONY IN ENAMELLED HOLLOW-WARE*

IN a special report (No. 29) issued by the Ministry in 1925 (*cf.* ANALYST, 1925, **50**, 133) on the solubility of glazes and enamels used in cooking utensils, attention was drawn to the possible toxic effect of antimony oxide. Since this report was published several outbreaks of poisoning, affecting large numbers of people, have occurred (*cf.* Dunn, ANALYST, 1928, **53**, 532), and, in view of the possibility that further and still more serious outbreaks might occur, the Ministry issued a warning (Ministry of Health Memo. 171/Med. 1933; ANALYST, 1933, **58**, 226) that enamelled hollow-ware vessels obviously intended for other purposes may be dangerous if used for the preparation or storage of food or drink. Further enquiries have shown that antimony enamels are used also for cooking vessels, and although no cases of illness definitely diagnosed as antimony poisoning have been traced to the use of enamelled cooking vessels, there is the possibility of chronic impairment of health from the continued ingestion of small doses of antimony.

THE ENAMELLING OF HOLLOW-WARE.—The vessel is spun or pressed from sheet iron and coated with a frit composed of some or all of the following ingredients: Borax, felspar, quartz, fluorspar, cryolite, lime, magnesia, sodium nitrate, which are mixed with water and china clay, and an opacifying agent. It is then dried and the coating is fused on to the metal in the enamelling furnace. Tin oxide is widely used to render the enamel opaque, but owing to its high price has been largely replaced by antimony, in the form either of trioxide or of sodium metantimonate. The former is used in this country and on the Continent, a well-known brand being "Timonox," whilst the latter is used to a limited extent on the Continent under the name "Leukonin" (*cf.* Beck and Schmidt, *Z. Unters. Lebensm.*, 1928, **55**, 1; Abst., ANALYST, 1928, **53**, 302). Oxides of cobalt, iron, manganese, nickel, etc., are also introduced into the enamel according to the colour required. Antimony trioxide is almost invariably fritted with the enamel mixture, whereas sodium metantimonate is usually added in the mill. These facts have an important bearing upon the state of oxidation of the antimony in the finished enamel.

The amount of silica in the enamel is of primary importance in connection with the contamination of food by antimony. A low silica-content, with corresponding preponderance of bases or boric acid, renders an enamel easily corroded, whilst a "hard" enamel, with high silica-content is less readily attacked. Since, however, "hard" enamel is more difficult to frit, and requires a higher temperature in the enamelling furnace, it is more expensive to produce, and the tendency is to use "soft" enamels on ware not intended for cooking purposes.

STABILITY AND SOLUBILITY OF ANTIMONY OXIDES.—Antimony pentoxide, when heated at temperatures above 440° C., loses some of its oxygen and forms lower oxides. The tetroxide is stable at all temperatures up to that of the gas blowpipe. The trioxide melts at a red heat and, on further heating, partly volatilises. Sodium metantimonate, $Na_2O.Sb_2O_5.7H_2O$, becomes anhydrous at 350° C., and does not lose oxygen until temperatures above 1000° C. are reached. Commercial anhydrous metantimonate contains about 11 per cent. of sodium, but preparations with much less sodium than this (apparently mixtures of antimony pentoxide and sodium metantimonate) are sold for use in certain kinds of enamel.

Antimony trioxide and pentoxide and sodium metantimonate are all more or less soluble in tartaric acid solutions. A fairly accurate separation of the trioxide from the other two oxides may be effected by treatment of the mixture at room

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* By G. W. Monier-Williams, O.B.E., Ph.D., F.I.C. Reports on Public Health and Medical Subjects. No. 73, pp. 18. H.M. Stationery Office, 1934. Price 4d. net.

temperature with 2 N hydrochloric acid, in which the pentoxide is only slightly soluble.

The Toxicity of Antimony Compounds.—Some of the recorded observations appear to be rather contradictory, but it seems clear that only soluble compounds of tervalent antimony are definitely and actively toxic. Soluble compounds of quinquevalent antimony are relatively harmless, although probably not absolutely non-toxic. Insoluble compounds of antimony in either state of valency appear to be relatively harmless.

The Action of Tartaric Acid Solutions on Enamelled Hollow-ware.—In the experiments described, samples of wrought hollow-ware, obtained in the course of visits to various factories, were tested with boiling 2 per cent. tartaric acid solution, 500 ml. of which were poured into the vessel and left for an hour, with occasional stirring. The solution was then poured off and diluted with water to 500 ml., and aliquot portions were used for the determination of total antimony and tervalent antimony. Details of the procedure are given.

State of Oxidation of Antimony in Enamels.—The method of determination of the trioxide and pentoxide is described in detail, and a table is given of the results obtained with 11 samples of hollow-ware. The figures indicate that when antimony trioxide is used in the enamelling process 50 per cent. or more becomes oxidised to higher oxides, owing probably to the presence of nitrates in the frit-mixture, and to absorption of oxygen from the air. When used as sodium metantimonate in the mill the antimony is partly reduced to trioxide, but the greater part remains in the quinquevalent state. In general, both oxidation and reduction of antimony compounds may occur in the fritting furnace. Antimony compounds added in the mill remain, for the most part, unaltered.

General Considerations.—Although the use of antimony in hollow-ware might be brought under control by (*a*) marking or labelling enamelled goods containing antimony, (*b*) applying a solubility test, or (*c*) allowing only the pentoxide or its compounds to be used, it is doubtful whether these measures would be entirely effective, and it is suggested that total prohibition of antimony in hollow-ware might be found to be in the best interest both of the public and of the trade.

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

The greater portion of the routine work of the Government Analyst's Department is provided by the Monopolies Department, and is concerned with the protection of revenue. It consists in the examination of opium, chandu, chandu dross, imported or locally distilled liquor, toddy and deleterious drugs. Work is also done for other Government departments, including the examination of exhibits from the Police Department. The Government Analyst (Mr. J. C. Cowap) gives details of all work undertaken in the main laboratory at Singapore and in the Penang branch laboratory. The total number of samples examined in the former laboratory was 14,345, and in the latter 3550.

Composition of Singapore Milk.—With the assistance of the Chief Health Officer, 129 samples of fresh cows' milk were taken for analysis under conditions which ensured the integrity of the milk and the completeness of the milking, the object being to attain a knowledge of what the quality of fresh milk sold in Singapore ought to be. The samples were taken from the mixed milk of small herds of cows (numbering from two to twelve), such as are kept by the usual milk-seller. The average figures were:—Sp.gr. at 15·5° C., 1031·5; fat, 5·13 per cent.; solids-not-fat, 9·42 per cent. The highest figure for fat was 9·3 per cent. (from the mixed milk of two cows) and the lowest 1·4 per cent.—also from the mixed milk of two cows.

Six samples of buffalo milk, similarly taken, gave as average figures:—Sp.gr., 1029; fat, 8·5 per cent.; solids-not-fat, 9·8 per cent.

DELETERIOUS DRUGS.—Seventy-six exhibits were examined in cases of possession or importation of deleterious drugs. Most of these contained Indian hemp, but a number of medicines were found to contain morphine, and one large seizure consisted of a number of tins containing pure cocaine hydrochloride and other tins containing a mixture of cocaine hydrochloride with a synthetic cocaine substitute. This method of adulterating cocaine has not been previously met with in the Colony.

COUNTERFEIT COINS.—Exhibits were received in 14 cases connected with counterfeit coins. In some of these cases complete outfits were found for making coins from fusible alloys. The usual alloy is made from tin, lead and antimony, but one lot of coins was made from an alloy of zinc with copper and aluminium, and another lot appeared to have been made from chandu tubes.

Twenty-six Straits Settlements 10 cents pieces and five Netherlands India half-guilders were found to be made from a silver-copper alloy and were counterfeit.

In one case a large number of coins appeared to have been defaced on one side and to have been re-engraved. As they were of the correct fineness of genuine coins, it was presumed that they had been used as buttons and afterwards reconverted to their original purpose.

EVIDENCE FROM DEPOSIT ON FEET.—In an interesting case a man accused of possession of goods which had been stolen from a house was found to have adhering to the inside of each foot a heavy blackish deposit. He was brought for examination and the substance scraped from the feet when examined microscopically was seen to consist of masses of two kinds of blue-green moulds, which were identified with moulds growing on the wall of the house from which the property had been stolen. Photomicrographs of the two were identical, and the man was convicted of house-breaking.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Contents of Phosphorus, Sulphur, and Alkalis in Hens' Eggs. J. Grossfeld and G. Walter. (*Z. Unters. Lebensm.*, 1934, **67**, 510–529.)—In agreement with published data, the yolk of the hen's egg contains, on the average, 1·42 per cent. of P_2O_5 or 2·78 per cent. on the dry matter, whereas the white contains 0·036 per cent. (0·28 on dry matter). The P_2O_5 of the lecithin amounts to 1·01 per cent. of the natural, or 1·98 per cent. of the dried yolk. One part of total P_2O_5 corresponds with 70 parts of yolk or 36 parts of dry yolk, and with 189 (50) parts of natural (dry) egg-contents. Similarly, 1 part of lecithin-P_2O_5 corresponds with 99 (50) parts of natural (dry) yolk or with 277 (73) parts of natural (dry) egg-contents. The ratio of total to lecithin-P_2O_5 is 1·41 for the yolk and 1·47 for the total egg-contents. In determining the total phosphoric acid, and in the conversion of the extracted lecithin into phosphate, good results are obtained by incineration in presence of magnesium acetate. For extracting the lecithin, practically equal yields are obtained by using either alcohol, a mixture of 4 parts of benzene with 1 part of alcohol, *iso*propyl alcohol, propyl alcohol, or methyl alcohol.

Calculation of the sulphur-contents of yolk and white from those of the various proteins present gives results agreeing with those of actual determinations. For egg-white the mean percentage of sulphur is 0·212 (1·67 on dry matter), and for yolk 0·222 (0·436 on dry matter). By simple incineration, even in presence of alkali, considerable loss of sulphur is incurred, and many incorrect published data have resulted therefrom. Good results are obtained after preliminary fusion with potassium hydroxide and nitrate in a silver crucible.

The average percentages of potassium and sodium are 0·112 and 0·045 respectively in the fresh yolks, and 0·153 and 0·179 respectively in the white. For determining potassium, the perchloric acid method, following fusion with barium acetate and treatment of the solution of the fused mass with baryta, proves satisfactory. The sodium may be determined, either indirectly in the same solution, or by incinerating a fresh quantity of material with magnesium acetate and applying Barber and Kolthoff's method (ANALYST, 1928, **53**, 456).

T. H. P.

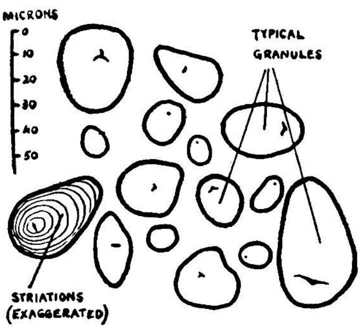
Colorimetric Determination of Manganese in Flours and Breads. P. Bruère. (*Ann. Falsificat.*, 1934, **27**, 150–157.)—The colorimetric determination of manganese furnishes information additional to that given by the ash determination in flours, and more particularly for breads suspected of addition of inferior products. It has been found that, calculated on 100 grms. of the dry material, 0·7 mgrm. of manganese is present, on the average in the wheat grain albumen, 13 mgrms. in the envelope and 19 mgrms. in the germ, giving a mean total of 2·881 mgrms. for the whole grain of average weight (weight of 1000 grains about 50 grms.). In the albumen (*i.e.* the central part of the grain) only about 0·4 mgrm. per 100 grms. is present, whereas the periphery has about 3 times as much; the external zone of the envelope (about 38 per cent.) contains much less manganese than the internal zone. To determine the proportion of manganese present, the white ash from 10 grms. of flour or 5 grms. of offal, is taken up with 10 ml. dilute (1:4) nitric acid, the mixture is filtered through an asbestos plate into a pyrex tube, the boiled water used for washing being added to the filtrate, and 5 drops of 0·1 *N* silver nitrate solution are added as catalyst, followed by 1 to 2 dgrms. of finely powdered potassium persulphate. The mixture is gradually heated to boiling, and as soon as the gas has been driven off, 20 ml. of water are added. The colorimetric determination is made at once either by comparison in a colorimeter with a solution of potassium permanganate of known strength, or with the aid of a colour-scale prepared from a solution of manganese sulphate (4·054 grms. to 4 mols. of water per litre), diluted when required. D. G. H.

Detection of Flour from Denatured Wheats. Identification of the Colouring Matter. J. Meyer. (*Ann. Falsificat.*, 1934, **27**, 174–175.)—In order to detect wheat flour which has been denatured with the aid of methylene blue or eosin, 25 to 30 grms. of the flour are spread out in an even layer, 3 mm.

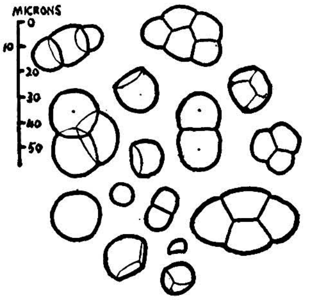
thick, on a glass plate, compressed by means of a white paper to a layer about 1 mm. in thickness, and moistened with 25 ml. of a mixture of 70 parts of 95 per cent. alcohol, 10 parts of glycerin and 20 parts of water, applied to the centre of the flour by means of a pipette with a fine jet. After 15 minutes' contact the slightest trace of colouring matter becomes apparent as a fresh stain of blue or pink, and such stains are best seen by examining the layer of flour by transmitted light. Occasionally the accidental presence of the débris of coloured vegetable fibres will give rise to different coloured stains. Examination under the microscope may then be necessary. By comparison with a type sample of flour similarly treated, the addition of lower grade flour to high grade flour may be detected.

D. G. H.

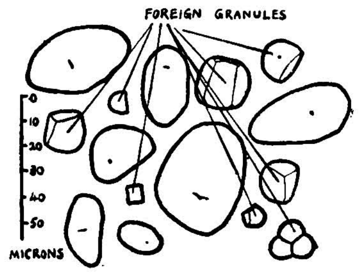
"Marble" Arrowroot. P. H. Jones. (*Food,* 1934, **3**, 225–228.)—Arrowroot has been defined by the Government of St. Vincent as "the separated and purified starch from the rhizomes of the plant known as *Maranta arundinacea,*" and this is the definition ordinarily accepted in the trade. During the war extensive adulteration of arrowroot with sweet potato starch was undoubtedly practised, but of late years there have been reports of the presence in arrowroot of small and varying quantities of a starch similar to sweet potato starch. The difficulties of accounting for the presence of sweet potato starch led to a search for a possible adulterant starch having similar truncated granules. It was found that a bulb-shaped tuber known as "marble" arrowroot grew in some plantations, and since it was thought by the planters to be an arrowroot, it was pulped with the true arrowroot, and thus gave rise to the small varying amounts of "sweet potato" reported. The granules of this starch are truncated, but rather smaller than those of true arrowroot (10–30μ).* The "marble" arrowroot bulb has been identified at Kew as *Myrosma cannifolia* (synonym *Calathea myrosma,* Lindley), and Professor Cheeseman of Trinidad reported it as belonging to the *Marantaceae,* but not of the genus *Maranta,* and therefore not an arrowroot. The plant grows wild in St. Vincent, Guiana and Brazil. Steps are now being taken to have this "marble" arrowroot eradicated, so that, in future, it shall not render imports liable to be condemned under the Food and Drugs Act. (*Cf.* p. 482.) D. G. H.



Maranta Starch



"Marble" Arrowroot Starch



Maranta Starch containing "Marble" Arrowroot Starch

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* These diagrams were drawn for THE ANALYST by Mr. A. H. Leather.—EDITOR.

Composition of the Glycerides of Coffee-Bean Oil. R. O. Bengis and R. J. Anderson. (*J. Biol. Chem.*, 1934, **105**, 139–151.)—The authors (*J. Biol. Chem.*, 1932, **97**, 99; Abst., ANALYST, 1932, **57**, 579) have shown that the unsaponifiable matter of the coffee-bean oil consists largely of a crystalline substance named kahweol, and that ordinary phytosterol is present only in small amounts in this fraction. A report is now given which deals with the composition of the oils obtained by extraction from the natural raw bean, the freshly roasted, and the stale roasted coffee-bean, and with the component fatty acids of the glycerides. Previous work by various authors is briefly discussed. The results show that there is no appreciable loss or change in the amount of fat of coffee-beans on roasting or ageing. The fragrant odour and flavour of the fat from freshly-roasted coffee disappear on ageing, and are replaced by an unpleasant rancid odour. A distinct increase in the water-soluble volatile acids occurs in the fat from the stale roasted beans. The unsaturated fatty acids, representing about 52 to 54 per cent. of the total acids, are composed approximately of equal parts of oleic and linolic acids. The solid saturated fatty acids consist mainly of palmitic acid, but small amounts of stearic acid and a tetracosanic acid are also present. An unsaturated, optically active, hydroxy acid of high molecular weight was present in the liquid acid fraction of all of the three fats examined. The oil contains a very small amount, (about 0·1 per cent) of phosphatid, which can be precipitated by acetone. The following results were obtained in the analyses of oils extracted from the beans with petroleum spirit:

	Fat extracted Per Cent.	Iodine value (Hanus)	Sapon. value	Reichert-Wollny value	Unsap. matter Per Cent.	Total fatty acids Per Cent.	Liquid acids Per Cent.	Solid acids Per Cent.	Acetone-insol. phosphatid Per Cent.
Green beans	81·1	97·8	179·3	0·56	9·0	86·5	52·3	39·4	0·1
Freshly roasted	90·4	96·0	172·1	0·86	10·2	87·0	54·4	37·5	0·08
Stale roasted	86·3	95·6	171·9	1·97	9·65	86·7	54·5	37·4	0·21

P. H. P.

Determination of Starch in Paprika adulterated with Flour. D. Köszegi and N. Tomori. (*Z. Unters. Lebensm.*, 1934, **67**, 538–541.)—The finely-ground paprika is passed through a fine cloth sieve, and 5 grms. are dried for 1 hour at 100° C., and then extracted with ether for 3 hours in a Soxhlet apparatus. The oil-free residue is transferred to a 100-ml. centrifuge tube, in which it is well mixed with water at 35° C., and centrifuged at 4000 revolutions per minute. After removal of the clear aqueous solution, this operation is repeated six times. The final residue is thoroughly ground in a porcelain mortar with 10 ml. of water, 40 ml. of concentrated hydrochloric acid (sp.gr. 1·19) being added gradually during the grinding. After 30 minutes, the contents of the mortar are transferred, with the help of 25 per cent. hydrochloric acid, to a 200-ml. measuring flask, and made up to volume with 10 ml. of 4 per cent. sodium phosphotungstate solution and 25 per cent. hydrochloric acid. After filtration, the clear liquid is polarised (as soon as possible) in a 2-dm. tube. The number of grms. of starch per 100 ml. of solution is given by $100\alpha \div 202l$, where α is the observed angular rotation and l the length of the observation tube in dm. [*i.e.* (2)]. Multiplication of the resulting number by 40 gives the percentage of starch in the paprika. This percentage must be diminished by 1·1, since, when treated as above, pure paprika gives a solution with a rotation of 0·1 to 0·12°, corresponding with 1·1 per cent. of starch. Test determinations on mixtures of paprika with maize-, wheat-, and rye-meals in various proportions gave satisfactory results. T. H. P.

Effect of Wrapping Material on the Fat of Fatty Foods. I. Contact Wrappers, Vegetable Parchment, Greaseproof Paper. II. The Effect of Sunlight passing through Transparent Wrappers of Various Colours (Cellophane) and Some Transparent Papers. W. L. Davies. (*J. Soc. Chem. Ind.*, 1934, **53**, 117–120T; 148–150T.)—I. The investigation of the copper- and iron-contents of vegetable parchment from various sources; of greaseproof paper, and of the wood cellulose pulp used for the manufacture of vegetable parchment (37 samples in all), showed that hard neutral vegetable parchment from British and Continental sources, and also wood cellulose pulp, contained on an average 22 p.p.m. of copper and 50 p.p.m. of iron. Practically no copper or iron was added during manufacture, except in the case of loaded samples, and on an average one-seventh of the iron and one-tenth of the copper of the hard neutral products were water-soluble. At p_H 5·6 about half the copper and one-seventh of the iron of British parchments were soluble in acetate buffer, but about 44 per cent. of the iron of Continental samples; at p_H 4·6, 42 to 87 per cent. of copper and 30 to 58 per cent. of iron were soluble. On the whole, the solubilities for soft parchments and for greaseproof paper were higher. In experiments designed to intensify the conditions necessary to cause fat autoxidation, it was found that peroxide formation was greatest with cotton wool, but with glass wool, vegetable parchment and sulphite pulp the rates were very similar. It appears that, in spite of the high content of iron and copper of hard neutral parchment, the effect of the metals is not appreciable within the range of acidities found in fatty foods during the usual storage time.

II. Eleven samples of variously-coloured cellophane were examined by actinometric reagents and by studying the rate of autoxidation of butter-fat and of the fat of biscuit meal wrapped in the samples. The samples divided themselves into 3 classes: (i) with no appreciable absorption of the chemically active rays, autoxidation consequently occurring practically as with direct exposure (colourless, light blue, pink, orange and lemon cellophanes); (ii) samples showing considerable absorption, and some autoxidation of the wrapped fat, but with evidence of a slow actinic effect (heliotrope and light green); and (iii) samples with complete, or nearly complete, absorption, and consequently with no appreciable increase of the peroxide oxygen of the wrapped fat (deeply coloured samples, green, blue, brown and red). Vegetable parchment allowed very little actinic light to pass; greaseproof paper fell into class (ii), and transparent papers were almost completely transparent to the active rays. Wax paper was opaque to active rays, but, in contact with dry fatty foods, volatile products of autoxidation of the wax appeared to initiate autoxidation of the fat of the wrapped food. The cellophanes showed a connection between the rate of autoxidation of the wrapped fatty material and the intensity of colour, irrespective of the colour of the sample. Absorption of the chemically active rays was thus co-relative with depth of colour and extinction coefficient, with the absorption in the region 400–500$n\mu$ by one thickness, and with the rate of increase of extinction by increasing the number of thicknesses of the cellophane. D. G. H.

Colorimetric Determination of Cantharidin. G. Denigès. (*Compt. rend.*, 1934, **198**, 1783–1785.)—When heated and shaken with formaldehyde and concentrated sulphuric acid, cantharidin gives a brown to black colour, and the reaction will detect 0·01 mgrm. of cantharidin. For comparative tests a series of standards is prepared by using increasing quantities of an acetic acid solution of cantharidin of such a strength that 1 drop corresponds with, say, 0·05 mgrm. of cantharidin, and adding to each the same volume of sulphuric acid. The sample should be diluted, if necessary, but the colorimeter comparison should then be made quickly, as the brown substance, which is in an unstable colloidal state, coagulates after a time. Other substances may give a brown colour in the presence of sulphuric acid, but cantharidin does so only in the presence of formaldehyde. The method may be used directly on chloroform decoctions of vesicant insects. After identification of the micro-crystals the quantitative determination may be made on an aliquot part of the solution. D. G. H.

Biochemical

Composition of Sweat. B. A. McSwiney. (*Lancet*, 1934, **226**, 641.)—Water is lost from the skin in two ways—by evaporation from the epithelial surface and by secretion through the sweat glands. The sweat may be strongly hypotonic in comparison with blood plasma, yet may remove what may be large amounts of sodium chloride from the body. Under normal conditions 600 to 700 ml. of sweat are evaporated from the skin in 24 hours. The constituents of sweat are very variable. The following table gives the average values calculated from the examination of 14 male and 10 female specimens:

		Mgrms. per 100 ml.				
Subject	p_H	Ammoniacal nitrogen	Urea	Amino-acid nitrogen	Glucose	Chlorides (NaCl) Grms. per 1000 ml.
Female	6·57	6·0	19·23	6·5	20·0	3·00
Male	6·14	4·7	21·44	5·0	12·6	3·70

Traces of creatine and creatinine have been found, and lactic acid is present in amounts not greater than 120 mgrms. per 100 ml. Examination of the sweat shed by rheumatic subjects shows no marked divergence from the normal. The secretion of sweat is under control of the nervous system, the sweat glands being innervated by sympathetic fibres, and the nervous mechanism may be called into action by central stimuli, by reflex action, or by peripheral stimuli. Adrenaline has no action on the glands, whilst pilocarpine excites and atropine paralyses them. Recent work suggests that the impulses are chemically transmitted by acetylcholine, liberated at the nerve-endings and acting on the sweat glands. P. H. P.

Influence of Fluorine Ingestion upon the Nutritional Qualities of Milk. P. H. Phillips, E. B. Hart and G. Bohstedt. (*J. Biol. Chem.*, 1934, **105**, 123–134.)—Nutritional studies on the inclusion of small but constant amounts of fluorine in the dietaries of different species of animals have shown that the practice is fraught with considerable danger. Since fluorine-bearing mineral supplements are in use for feeding dairy cattle, milk might thus have a sufficiently increased fluorine-content to produce harmful effects. Studies were made to determine whether the nutritional qualities of milk were influenced by different levels of fluorine intake, such as might be encountered in ordinary dairy cattle-feeding. The problem was approached in two ways: (i) by a biological test of the milk from controls and from rock phosphate-fed Holstein cows, and (ii) by a systematic study of the fluorine-content of the milk produced by these cows. The results show that mineralised milk samples from individual cows may cause variable milk consumption in rat-feeding experiments; the cause of such variation is not clear. No difference was observed in the biological reaction of rats given normal milk, as compared with those fed with milk from cows receiving an added source of fluorine. Fluorine determinations of milk from cows receiving no added fluorine in their normal ration and from those receiving added sources of fluorine showed that they were not widely different with respect to their fluorine-content. The range of fluorine in normal milk was found to be 0·05 to 0·25 mgrm. of fluorine per litre, with an average value of 0·138 mgrm. The lactation (first, second or third) or period of lactation was without effect on the fluorine-content of the milk. Fluorine added to milk diets resulted in a higher residual fluorine in the body ash. The storage of fluorine was not proportional to the total fluorine intake. Apparently, a mechanism of elimination operates beyond certain threshold limits. No noticeable difference was demonstrated between the residual fluorine of the body ash of rats fed with milk from cows receiving no added source of fluorine and those fed with milk from cows receiving an added source of fluorine. Diets with traces of fluorine ranging from 4·5 to 132·0 micro-grms. of fluorine per rat per day produced no detectable toxicosis; these levels of fluorine intake are without effect, and it seems likely that no stimulation of physiological processes can be attributed to small non-toxic doses of fluorine. The fluorine-content of milk is comparatively difficult to influence by dietary means. This does not preclude the possibility that the use of a more soluble form of fluoride in equal or larger doses might increase the fluorine-content of milk. It is apparent that fluorine in concentrations greater than 1 part in 10 in the diet has no essential function in the metabolism of the rat.

P. H. P.

Influence of Breed and Diet of Cows on the Carotene and Vitamin *A* Content of Butter. C. A. Baumann, H. Steenbock, W. M. Beeson, and I. W. Rupel. (*J. Biol. Chem.*, 1934, **105**, 167–176.)—Spectroscopic determinations have been made of the carotene and vitamin *A* content of butter-fat from cows of various breeds on high and low carotene diets. Definite breed differences were noted. On the winter ration, average carotene values ranged from 4·3 micrograms per grm. for Holstein butter to 7·8 micrograms per grm. for Guernsey butter; vitamin *A* ranged from 5·1 micrograms per grm. for Guernsey butter to 10·1 micrograms per grm. for Holstein butter. On the green feed ration, averages for carotene ranged from 5·5 micrograms per grm. for Ayrshire butter to 17·0 micrograms per grm. for Guernsey butter; vitamin *A* ranged from 8·5 micrograms per grm. for Guernsey butter to 15·1 micrograms per grm. for Holstein butter. When butters from different breeds on the same diet were compared, inverse relations between the carotene and vitamin *A* were revealed; *i.e.* when carotene was high, vitamin *A* tended to be low, and *vice versa*. Individual variations between members of the same breed on the same diet were of the order of 100 per cent. When the carotene intake of the cow was increased there was an increase in both the carotene and vitamin *A*-content of the butter fat. Calculations indicated that 3·3 per cent. of the vitamin *A* ingested on a low carotene ration was secreted in the milk; on a high carotene ration only 1·3 per cent. was secreted. The results indicate that the proportion of the total vitamin *A* activity of butter due to carotene depends mainly upon the breed from which the butter is obtained. Vitamin *A* is of primary importance only in butter from those breeds which produce a butter of relatively low pigment-content. In a highly coloured butter most of the activity may be due to carotene. The results also emphasise the inadequacy of the natural colour of butter as an index of vitamin potency. P. H. P.

Differences between Biologically Active Substances before and after Isolation from the Raw Material in which they occur. H. I. Waterman and C. Van Vlodrop. (*Rec. Trav. Chim. Pay-Bas*, 1934, **53**, 670–671.)—Although it was found possible to recover carotene, dissolved in red or colourless palm oil, by distillation in a cathode light vacuum with internal condensation (*Rec. Trav. Chim. Pays-Bas*, 1933, **52**, 895), and consequently to concentrate solutions of carotene, yet when natural palm oil, or palm oil concentrate, was submitted to a similar treatment no concentration of colouring substances in the distillate could be obtained. However, the distillate from natural palm oil, on re-distillation under the same conditions, behaves like the carotene preparation dissolved in oil, the residue being freed to a large extent from the colouring substances. Concentration of the pigment practically without decomposition thus becomes possible. It is surmised that carotene does not occur as a free molecule in natural palm oil.

D. G. H.

Relation of Reducing Value and Extent of Browning to the Vitamin *C* Content of Orange Juice Exposed to Air. M. A. Joslyn, G. L. Marsh and A. F. Morgan. (*J. Biol. Chem.*, 1934, **105**, 17–28.)—It is known that orange juice exposed to atmospheric oxygen will gradually decrease in its reducing value towards iodine and also towards 2, 6-dichlorophenolindophenol; if the exposure is continued, browning occurs and increases in intensity. Studies were undertaken (i) to determine whether any change in vitamin *C* is involved in the browning of orange juice, and (ii) to compare the iodine titration with the indophenol titration as an indication of the changes in vitamin *C* content of orange juice during oxidative deterioration over a long period. Two lots of navel orange juice and one lot of Valencia orange juice were used, and it is shown that loss of vitamin *C* accompanies decrease in the iodine-reducing and indophenol-reducing value of orange juice, and occurs at about the same rate; the correlation of titre and antiscorbutic value is definitely better with Valencia than with navel orange juice. The extent of browning is parallel to the extent of loss in vitamin *C*, so that the latter is either involved in browning or it is destroyed simultaneously. Navel orange juice has a higher concentration of reducing substances than Valencia orange juice, and probably has more reducing material other than ascorbic acid; 1 ml. of navel orange juice is the equivalent of about 1·5 ml. of Valencia juice. The decrease in reducing value of orange juice which occurred during freezing storage was more marked in partly oxidised juice. There is little choice between the indophenol titration and the iodine titration for the determination of changes in vitamin *C*-content during prolonged oxidation of orange juice, but the iodine titration is easier to carry out and can be more readily duplicated. P. H. P.

Toxicological and Forensic

Spectrum of Haematoporphyrin and its Significance in the Recognition of Traces of old Blood-stains. M. Wagenaar. (*Pharm. Weekblad,* 1934, **71,** 478–482.)—The fluorescence and spectroscopical properties of haematoporphyrin may be used as a means of identifying old bloodstains (*cf.* ANALYST, 1930, **55,** 405). The action of sulphuric acid on the non-fluorescent haematin is to convert it into haematoporphyrin, which is fluorescent and appears purple in strongly acid solutions and dark violet in the presence of alkali. A fluorescence microscope and a micro-spectrometer are desirable for the study of small quantities of material. In the latter case a few threads are treated on a microscope slide with as much strong sulphuric acid as can be removed from the bottle on a straight platinum wire. A cover-slip is then placed in position, and a drop of acetone or of ethyl acetate is applied to its edge and allowed to flow under it. Local heating thus probably results, and both the extraction process and the formation of haematoporphyrin are stimulated and a good spectrum results (principal lines at 598 and 550$m\mu$); if a drop of ammonia is then drawn under the cover-slip by means of a strip of filter paper, the principal lines seen are at 615, 574, 544, and 509$m\mu$. J. G.

Organic Analysis

New Reactions of Aldehydes and Ketones. Synthesis of Thiodiazolines from Ketones. (Mlle) A. Lacourt. (*Bull. Soc. Chim. Belg.*, 1934, **43,** 206–210.)—Aldehydes and ketones readily condense with thiohydrazides to form substituted thiodiazolines, which are easily purified. The reaction is general for aliphatic and cyclic ketones and acetophenones, but is given by benzophenones, camphor and fenchone so slowly that the thiohydrazide is decomposed by the prolonged action of the catalyst employed. When a solution of 3 grms. of α-phenyl-β (α-thionaphthyl)-hydrazine in 3 ml. of acetone is heated for 2 minutes with 10 drops of a 20 per cent. solution of hydrochloric acid in aqueous alcohol, 2:2′-dimethyl-3-phenyl-5-α-naphthyl-2:3-dihydro-1:3:4-thiodiazole, m.pt. 68° C., is formed. The other derivatives described were prepared similarly from: acetophenone and α-phenyl-β-phenylthioacetylhydrazine, m.pt. 120° C. (in 22 seconds); acetophenone and α-phenyl-β (α-thionaphthoyl) hydrazine, m.pt. 110° C. (20 secs.); cyclopentanone and α-phenyl-β-thiobenzoylhydrazine, m.pt. 94° C. (20 secs.); cyclopentanone and α-*p*-bromophenyl-β-thiobenzoylhydrazine, m.pt. 79° C. (20 secs.); cyclopentanone and α-phenyl-β (α-thionaphthoyl) hydrazine, m.pt. 98° C. (20 secs.). All of these heterocyclic derivatives dissolve in concentrated sulphuric acid, giving yellow or greenish-yellow solutions which, on addition of solid sodium nitrite, yield intense blue or violet colorations. Addition of a few drops of a 10 per cent. solution of silver nitrate in aqueous alcohol to saturated alcoholic solutions of the compounds gives a white precipitate; this usually begins to undergo reduction within a few minutes. T. H. P.

Detection of Carbon Tetrachloride in Chloroform. G. Ciogolea. (*J. Pharm. Chim.*, 1934, **126**, 377–383.)—Sivadjian's method (*ibid.*, 1929, **121**, 434) is satisfactory only when carried out exactly as follows: To a mixture of 5 ml. of a 1 per cent. solution of pyrocatechol in alcohol with 2 ml. of the chloroform in a test-tube, 0·5 ml. of sodium hydroxide solution (French Codex) is added so as to mix as little as possible with the alcoholic liquid. Powdered copper or commercial bronze powder (0·3 to 0·35 grm.) is then added, and the test-tube is heated for exactly 2 minutes in a water-bath at 100° C. The tube is at once cooled under the tap, 1 ml. of concentrated hydrochloric acid and 1 ml. of distilled water are added, the tube is shaken gently, and the liquid is allowed to stand for a few moments and then filtered. If the chloroform is pure, the filtrate is straw-yellow. If it contains from 0·25 to 0·5 per cent. of carbon tetrachloride, the colour is straw-yellow with a slight orange tint. With 0·5 to 1 per cent. of the tetrachloride, the filtrate is orange-yellow, and with more than 1 per cent., pink. A check test should always be made with anaesthetic chloroform. A modification of the method described in the French Pharmacopoeia (1908) is suggested, but this method cannot be made as sensitive as that given above. T. H. P.

Studies on the Merino Fleece. I. Chemistry of Suint. M. R. Freney. (*J. Soc. Chem. Ind.*, 1934, **53**, 131–134T.)—For the author's purposes, suint is taken to comprise those substances in raw wool which are soluble in warm water and are separated from the other elements of wool by simple filtration. Suint is normally neutral or slightly alkaline, but occasionally definitely acid, and different samples vary greatly in ash- and nitrogen-contents. From 10 to 20 per cent. of the dry matter consists of fatty acids, including lactic, hippuric, and succinic acids in small proportions. The nitrogen- and ash-contents of normal suint are similar to those of human sweat, but a dried sample of human sweat contained much more chloride than suint. No positive tests for proteins were given by suints or by human sweat. Small amounts of urea and ammonia occurred in most of the suint samples, the presence of nitrogenous bases suggesting that protein was originally present but had suffered decomposition. The inorganic constituents have not been thoroughly investigated, but one suint was found to contain much potassium, with less sodium and very little calcium. Sulphate, carbonate, chloride, silica, and traces of iron and phosphate were observed.

For two samples of suint from Australian merino wools, the following results were obtained on the dry matter:

Reaction	South Australian alkaline Per Cent.	Victoria neutral Per Cent.
Volatile acids	9·5	1·1
Higher fatty acids	2·0	13·8*
Organic matter precipitated by lead acetate	—	24
Organic matter not ,, ,, ,, ,,	—	4·7
Ammonia	0·2	—
Hippuric acid	0·13	1·4
Total nitrogen	2·2	2·3
Succinic acid	—	1·4
Lactic acid	—	0·32
Ash	50	48

* Iodine value of these acids, 9·4.

T. H. P.

Inorganic Analysis

Determination of Small Amounts of Bismuth, Antimony, Tin, and Molybdenum in Copper (Spectrographic Method). B. Park. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 189–190.)—Bismuth, antimony, tin, and molybdenum, present in minute amounts in copper, may be quantitatively collected by co-precipitation on manganese dioxide from bromide-bromate solution, as follows: A 100-grm. sample of the copper is dissolved in 400 ml. of concentrated nitric acid, and the solution is evaporated to dryness on a steam-bath. The residue is dissolved in 1 litre of water, the solution is heated to boiling, and *N* sodium carbonate solution is added until a slight permanent precipitate is formed, which is then re-dissolved by the addition of 1 ml. of nitric acid. To the boiling solution are added 10 ml. of potassium bromide solution (20 per cent.), and 10 ml. of potassium permanganate solution (3 per cent.). The liberated bromine is removed by boiling for 30 minutes, and the precipitated manganese dioxide is filtered off and washed with a little water. The precipitate is combined with a second precipitate obtained by treating the solution with potassium bromide and permanganate as before, and dissolved in 50 ml. of concentrated hydrochloric acid. This solution is concentrated to 30 ml., neutralised with ammonia, acidified with 1 ml. of concentrated hydrochloric acid, diluted to 100 ml. and saturated with hydrogen sulphide. The sulphides are filtered off, washed with water, and dissolved in a hot mixture of 25 ml. of concentrated nitric acid and 10 ml. of hydrochloric acid. The solution obtained is evaporated to 5 ml., and 10 ml. of concentrated hydrochloric acid are added; the liquid is evaporated to 3 to 4 ml. and diluted to 5 ml. (Nothing is mentioned as to the possibility of loss of tin in these evaporations.—*Abstractor.*) The metals are determined by means of the arc spectrum of portions of the solution absorbed in graphite electrodes according to the method of Nitchie (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 1). The fact that the precipitate obtained by a third treatment with bromide and permanganate of the copper solution, to which 2 mgrms. of each of the elements in question had originally been added, was spectroscopically free from them, was taken to prove the completeness of precipitation in the above method. Eleven different samples of refined copper gave the following results: Antimony, nil to 0·002 per cent.; tin, 0·00004 to 0·0015 per cent.; bismuth, <0·00001 to 0·0045 per cent.; molybdenum, nil to 0·0005 per cent. S. G. C.

Qualitative Separation of Cobalt from Nickel by means of Ammonium Phosphate. H. Wunshendorff and P. Valier. (*Bull. Soc. Chim.*, 1934, **1**, 85–90.)—Within a narrow range of p_H values and concentration of ammonium salts, cobalt phosphate is relatively insoluble, whilst nickel remains in solution. The following method is proposed for testing the mixture of cobalt and nickel sulphides obtained in the course of the qualitative group separations. The sulphides are dissolved in *aqua regia*, the solution is evaporated to dryness on a water-bath, and the residue is dissolved in the minimum of water. To a 2-ml. portion of the solution are added 1·5 ml. of 2 *N* ammonium carbonate solution, followed by 1·5 ml. of 2 *N* diammonium hydrogen phosphate solution. The liquid is heated to boiling and 20 drops of ammonia (sp.gr. 0·92) are added. The boiling is continued for 4 minutes, and the liquid is filtered without delay. If nickel is present, the filtrate is coloured a turquoise blue, and if cobalt is present, a violet precipitate remains on the filter. Quantities of the metals of the order of one-tenth mgrm. may thus be detected. S. G. C.

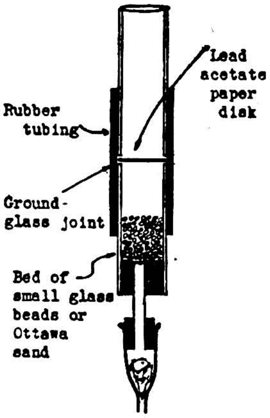
Separation of Potassium and Sodium as Iodides. L. Szebellédy and K. Schick. (*Z. anal. Chem.*, 1934, **97**, 106–116.)—The process is based on the solubility of sodium iodide and the insolubility of potassium iodide in a mixture of equal volumes of isobutyl alcohol and ether, both absolute. Chlorides and sulphates are converted into iodides by simple evaporation with hydriodic acid (sp.gr. 1·96); carbonates and nitrates are first converted into chlorides. Phosphates are not convertible, hence the phosphate ion must be removed by precipitation. The mixed salts (0·25 to 0·3 grm.) are dissolved in a few drops of water in a 50 ml. silica dish, and the solution is evaporated with hydriodic acid. The residue is dried for an hour at 125° C., cooled over sulphuric acid, and ground for 10 minutes with a small pestle under 5 ml. of isobutyl alcohol. Ether (5 ml.) is added, and the precipitate is left to settle for 3 minutes. The liquid is filtered through a small, close paper moistened with the alcohol. The insoluble residue is dissolved on the filter with 5 ml. of ethyl alcohol followed by 25 ml. of warm water. The washings are collected in the silica basin, and evaporated to dryness with a drop of hydriodic acid. The treatment of the residue is repeated, once if the mixture is poor, twice if rich, in sodium; if the potassium residue is small, the third extraction is carried out with 5 ml. of mixed solvent.

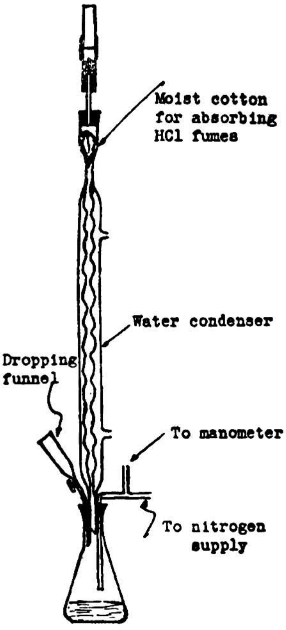
The sodium extract is evaporated to dryness in a wide, shallow weighing-bottle with ground-glass stopper, as sodium iodide is very hygroscopic. The salt must be dehydrated at 180° C. for one hour. Potassium iodide is not hygroscopic; it is dissolved in water, the solution is evaporated to dryness, and the residue dried like the sodium salt. The two alkalis may also be determined gravimetrically or volumetrically as silver iodide. In any case, a deduction of 0·0006 grm. is made from the calculated weight of Na_2O, and corresponding addition made to that of K_2O. If the amount of either alkali is very small, its identity should be proved. The advantages claimed are the direct determination of the sodium and the application to mixed sulphates after simple evaporation with hydriodic acid.

W. R. S.

Colorimetric Determination of Fluoride by means of a Photronic Colorimeter. L. V. Wilcox. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 167–169.)—Armstrong's method (*ibid.*, 1933, **5**, 300), which involves the bleaching action of fluoride on the coloured ferric acetylacetone compound, has been used, a photronic colorimeter being employed for effecting the colorimetric comparison. The light-measuring elements of the colorimeter consist of two Weston Photronic cells, and the intensity of the light transmitted through the solution is measured in terms of electrical resistance. For the construction of the colorimeter, which is of a somewhat detailed character, and the method of working, the original paper should be consulted. S. G. C.

Determination of Minute Quantities of Sulphide Sulphur. C. E. Lachele. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 200–201.)—The method involves the darkening of lead acetate-paper by hydrogen sulphide liberated by acid attack of the sample, an even degree of darkening of the paper being secured by allowing the gas to pass through a bed of sand or small glass beads before it reaches the paper. The sample is placed in the 1000-ml. flask of the apparatus (see Fig.), which is swept out with a stream of nitrogen; 50 ml. of hydrochloric acid (1 : 1) are added from the dropping funnel and the liquid is boiled, nitrogen being passed through it until all the sulphide has been evolved (time required is not stated). The lead





acetate paper is washed in distilled water and dried, and the stain is compared with standard stains obtained by evolving the sulphide from a suitable quantity of a standard steel. Pale stains may be compared in reflected light, but with darker stains examination in transmitted light is necessary. For amounts of sulphur between 0·008 and 0·08 mgrm., a lead acetate-paper disc 32 mm. in diameter is satisfactory; the accuracy is ± 0·002 mgrm. *Applications.*—The method has been employed for the determination of sulphide sulphur in raw and canned foodstuffs (no details are given), water, the tin coating of tinplate and the sulphide stain imparted to the inside of tinned containers by certain foods. In the case of the stain, this was dissolved off without appreciable attack of the tin, by immersion of the sample for 2 minutes in a boiling solution consisting of 4 parts of sodium hydroxide solution (1 per cent.) and 1 part of sodium silicate solution (40° Bé.), and the sulphur was determined in this solution. For determining the sulphur-content of the tin coating of tinplate, the specimen was immersed in sodium hydroxide solution (1 per cent.), and sprinkled with pieces of cupric oxide wire. The tin coating, excluding the underlying alloy layer, dissolved off in about two hours at the ordinary temperature, or in a few minutes when the liquid was heated; the liquid, after the stripping process, was transferred to the apparatus for the evolution and determination of the sulphur. S. G. C.

Analysis of Phosphate-bearing Silicates. A. Lassieur. (*Ann. Chim. anal.*, 1934, **6**, 197–202.)—When the proportion of phosphate is considerable, it is usual to effect the preliminary removal of phosphoric acid by precipitation as ammonium phosphomolybdate, and, as a consequence of this, it is necessary to eliminate the added excess of molybdenum remaining in the solution before proceeding with the determination of iron, aluminium, calcium, etc. The author recommends precipitating the iron, aluminium and calcium together by means of ammonium carbonate and ammonia, and removing the small quantity of entrained molybdenum in this precipitate by dissolving this in acid and precipitating with hydrogen sulphide. When the amount of phosphoric acid in the silicate is small, say, less than one-tenth of that of the iron and aluminium oxides present, it is possible to avoid the preliminary precipitation of the phosphate. The hydroxides of iron and aluminium may be precipitated with ammonia. The whole of the phosphoric acid is present in this precipitate as insoluble iron and aluminium phosphates, and calcium remains in solution. The precipitate is calcined, weighed, and taken up by fusion with potassium pyrosulphate; the iron oxide and phosphoric acid are determined in the solution obtained, and the aluminium oxide is found by difference. S. G. C.

Detection of Selenium and Tellurium. N. S. Poluektoff. (*Mikrochem.*, 1934, **15**, 32–34.)—(i) For the detection of selenium in the presence of tellurium, filter paper is treated with a drop of concentrated hydriodic acid (or potassium iodide solution and a drop of hydrochloric acid), and a drop of the acid test solution is placed in the middle of the moist fleck. If the black-brown fleck is then completely decolorised by sodium thiosulphate, no selenium is present. In the presence of selenium a red-brown fleck of elementary selenium remains. The limit of identification is 1γ of selenium (in 0·025 ml.), and the limit of concentration is 1 : 25,000. In the presence of tellurium the limit of identification is 2·5γ of selenium, and the proportion limit is Se : Te = 1 : 615.

(ii) Tellurium in the presence of selenium is detected as follows:—A drop of stannous chloride solution, a drop of 25 per cent. sodium hydroxide solution, and a drop of the alkaline test solution are mixed on a spot plate. In the presence of tellurous acid a black precipitate, or grey colour, appears. When very small amounts of tellurium are present the colour develops only after 1½ to 2 minutes, and a blank should be carried out. The limit of identification is 0·6γ of tellurium (in 0·025 ml.), and the limit of concentration is 1 : 41,000. For tellurium in the presence of selenium the limit of identification is 0·8γ of tellurium and the proportion limit is Te : Se = 1 : 100. J. W. M.

Determination of Selenium in Selenites, Selenates and in "Metallic Selenium." J. H. Van der Meulen. (*Chem. Weekblad,* **1934, 31, 333–335**; *cf. ibid.*, 1931, **28**, 348.)—(i) *Reduction.*—A mixture of 20 ml. of a 0·05 *N* solution of sodium selenite with 150 ml. of water, 15 ml. of a 2 per cent. solution of starch, 10 ml. of *N* potassium iodide solution and 10 ml. of 5 *N* hydrochloric acid is titrated after 1 minute with a 0·1 *N* solution of sodium thiosulphate. If the above quantity of starch is added at an early stage, it serves as a protective colloid, and prevents precipitation of the reddish-violet elemental selenium

$$(Na_2SeO_3 + 4KI + 6HCl = 2NaCl + 4KCl + 3H_2O + 2I_2 + Se);$$

the end-point, which is a change from brownish-red to a brighter and purer red, is then sensitive to 1 drop of solution.

(ii) *Bromo-iodimetric Oxidation.*—The selenite is oxidised to selenate by means of hypobromite, the excess of which is determined (without reduction of the selenate) by liberation of iodine from an iodide in the presence of a catalyst and a strong acid; thus, $Na_2SeO_3 + NaOBr = Na_2SeO_4 + NaBr$. A mixture of 40 ml. of a 0·05 *N* solution of sodium selenite, 10 ml. of a *N* solution of potassium bicarbonate and 25 ml. of 0·2 *N* sodium hypobromite reagent (prepared by mixing solutions of 16 grms. of bromine in 500 ml. of water and of 12 grms. of sodium hydroxide in 100 ml. of water and diluting to 1000 ml.) is diluted with 50 ml. of water; a bicarbonate (or boric acid) ensures rapid and complete oxidation. The iodine liberated after addition of 10 ml. of a *N* solution of potassium iodide, 5 ml. of 5 *N* hydrochloric acid, and a few drops of a solution of a molybdate, is titrated in the usual way with a solution of sodium thiosulphate. (iii) *Selenium Metallicum.*—The powdered selenium (3·96 grms.) suspended in 100 ml. of water is treated with 8 grms. of solid potassium bromate, the reaction being stimulated, especially towards the end, by gentle heat and, in the final stages, by the addition of a further 2 grms. of bromate. The mixture is cooled and diluted to 1000 ml., and 20 ml. of this selenate solution are mixed with 20 ml. of 2 *M* potassium bromide solution and 10 ml. of hydrochloric acid. The selenate is thus reduced to selenite, which is determined (*cf. supra*) with potassium iodide and starch. The respective results (as percentages of Na_2SeO_3) for technical sodium selenite and *Natrium selenosum puriss.* for the 3 methods were:—(1) 93·55, 97·75; (2) 93·88, 98·00; (3) 93·55, 97·75. J. G.

Microchemical

New Method of Preparative Micro-chemistry. J. Winckelmann. (*Mikrochem.*, 1934, **14**, 171–180.)—Permanent microscopic preparations of crystals and precipitates are made by covering the crystals with a thin film of collodion through which they can be washed without loss or disturbance, and finally mounting them in Canada balsam. The usual 6 per cent. collodion solution is used, or it may be diluted with a tenth of its volume of alcohol, or alcohol and ether. The method is illustrated by the formation and mounting of silver chromate. A small drop of 0·05 to 0·01 per cent. silver nitrate solution is placed on each of several clean microscope slides; one drop is left untouched, and to the others a trace of dilute nitric acid, or a trace of nitric acid and sodium or ammonium acetate is added. Then, into each of the drops is introduced a small crystal of potassium chromate. If the characteristic crystals appear at once, the solution contains too much silver, and the test should be repeated in greater dilution until a preparation is obtained in which not too many crystals are formed, and these are formed slowly and are well defined. The best preparation from the number of test drops is used for the final treatment. The drop is allowed to dry slowly until a crystal conglomerate of silver chromate and reagent is formed. This is covered with a thin layer of collodion, which may almost cover the whole slide. After this is dry a small drop of water (or wash liquid) is placed on the collodion over the preparation. The easily soluble salts soon dissolve and the drop can be removed by means of a small pipette with a rubber teat. This washing is repeated several times, and dilute alcohol may be used for the final washing. It is convenient to use a lens giving a magnification of about 10 during the washing. The drops of wash liquid must never be allowed to run over the edge of the collodion film, and, therefore, a level mounting table should be used. After washing, the preparation is allowed to dry in the air, and the excess collodion may then be cut away from the edges. The preparation is already fairly permanent, but it may be mounted under a cover glass and cemented with Canada balsam in the usual way. In this way permanent preparations are made for photography, or for measurement of size, crystal angle, and other physical properties. J. W. M.

Microchemistry of Euquinine. M. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 435–438.)—Quinine ethyl carbonate ($C_2H_5O.COO.C_{20}H_{23}N_2O$) forms colourless and odourless crystals melting at 91° C., and having a slightly bitter taste; when dissolved in dilute sulphuric acid they give (like quinine) a solution having a blue fluorescence. Such solutions also give the thalleioquin reaction (green colour with bromine water and ammonia), and it is stated that this test is best made in an atmosphere of chlorine. Warm sodium hydroxide decomposes solutions of euquinine, with the liberation of ethyl alcohol, which may be detected by the iodoform test, a crystal of material being warmed with a drop of the alkali on a microscope slide just beneath a watch glass containing cold water which serves to condense the alcohol produced. An alternative, but less reliable, modification of the reaction is to warm the solution to be tested with ammonia and a solution of iodine in potassium iodide solution, when a yellow colour develops, and, after a time, crystals of iodoform are formed and may be identified under the microscope. Euquinine is best obtained for identification by slow evaporation of a solution in a mixture of acetone and water, from which it separates as characteristic, well-formed columnar crystals. Addition of a slight excess of ammonia to a solution of euquinine in dilute hydrochloric acid produces an opalescence which dissolves on addition of a few drops of acetone, and on evaporation of this mixture fine characteristic rosette-shaped crystals result. If one drop of a solution of iodine in potassium iodide solution is added to a solution of euquinine in dilute hydrochloric acid, an amorphous precipitate results which dissolves immediately on the addition of a drop of acetone and reappears in the form of fine crystalline bundles during slow evaporation (herapathite reaction).

J. G.

Collected References. Micro-Determination of Nickel and Cobalt. Z. Stary. (*Mikrochem.*, 1934, **15**, 141–150.)—The various methods for the micro-determination of cobalt and nickel are briefly described, and, in all, 53 references are given. The methods include: electrolytic, gravimetric (of which for nickel the most important is the dimethylglyoxime method), volumetric, colorimetric and spectrographic methods. J. W. M.

Rapid Micro-method for the Determination of Uric Acid in Urine. P. Wenger, Ch. Cimerman and A. Maulbetsch. (*Mikrochem.*, 1934, **14,** 129–131.)—The usual macro-method, in which the uric acid is precipitated as ammonium urate, filtered, and determined by oxidation with $N/10$ iodine in alkaline solution, is carried out on 2 ml. instead of 100 ml. of urine. The Emich filter-stick, made of Berlin porcelain, is used for filtration. The sample is measured into a micro-beaker and treated with 6 drops of concentrated ammonia and 0·3 grm. of ammonium chloride, and, after standing five minutes, the mixture is filtered through the filter-stick, and the residue is washed three times with 1 ml. of wash liquid. The precipitate is washed down with 1 ml. of water and dissolved in acetic acid (1 : 10), added, drop by drop, until the solution is just acid. The filter-stick serves as a stirrer. After the addition of a little solid borax to render the liquid alkaline, the solution is titrated against $N/100$ iodine, starch being used as indicator. One ml. of $N/100$ iodine $\equiv$ 0·00084 grm. of uric acid, or n ml. $\times$ 0·42 $+$ 0·01 $=$ the quantity of uric acid in grms. per litre; 0·01 represents the correction for the slight solubility of ammonium urate. A determination can be completed in 15 minutes, as compared with 1½ hours for the macro method, and it gives equally accurate results. J. W. M.

Micro-Determination of Urea in Blood. P. Wenger, Ch. Cimerman, and A. Maulbetsch. (*Mikrochem.*, 1934, **14**, 132–140.)—Fosse's method (*Compt. rend.*, 1913, **157**, 948; 1914, **158**, 1076, 1432) of precipitation of urea with xanthydrol, as modified by Nicloux and Welter (*Bull. Soc. Chim. biol.*, 1922, **4**, 128) for 1 ml. of serum is used, except that instead of the liquid being filtered through a micro-Neubauer crucible, an Emich filter-stick of Berlin porcelain is used. The filter-stick and micro-beaker containing the precipitate are dried in a Pichler drier at 105°–110° C., and finally weighed on a micro-balance. Accurate results are obtained. The Allen and Luck method (*J. Biol. Chem.*, 1929, **82**, 696), in which titration replaces weighing was also used, but, instead of centrifuging the precipitate, it was filtered as before, using an Emich filter-stick. This simplifies the method and renders it more rapid, and the same degree of accuracy is obtained.

J. W. M.

Detection of Enzymes by "Spot" Tests. B. N. Sastri and M. Sreenivasaya. (*Mikrochem.*, 1934, **14**, 159–160.)—The method consists in mixing on a strip of fat-free filter paper (3 in. × ½ in.) a drop of the substrate solution and a drop of the test liquid, and leaving the paper (together with the necessary controls) for 30 to 60 minutes in a moist atmosphere under a bell-jar. The drop is then examined for the reaction products with the suitable reagents. Where a reducing sugar is released, Fehling's test is used, and a jet of steam is directed on to the spot to facilitate reduction. A brick-red or orange colour indicates that the enzyme was present.

Enzyme	*Substrate*	*Reaction*	*Remarks*
Diastase	0·5 per cent. soluble starch	Fehling's	Brick red or orange colour
Inulase	0·5 per cent. inulin	Fehling's	,, ,, ,, ,,
Invertase	0·5 per cent. sucrose	Fehling's	,, ,, ,, ,,
Emulsin	0·5 per cent. salicin	Fehling's	,, ,, ,, ,,
Emulsin	0·5 per cent. indican	Treated with alkali and exposed to air	Blue colour
Lipase	0·2 per cent. olive oil emulsion	Methyl red	Red
Butyrase	0·2 per cent. ethyl acetate in aqueous emulsion	Methyl red	Red
Urease	1 per cent. urea	Phenolphthalein	Pink
Phenolase	1 per cent. tincture of guaiacum	—	Blue colour
Tyrosinase	Tyrosine	—	Brown

Amylase and urease are best detected on the spot plate, when a drop of 0·5 per cent. soluble starch and a drop of the test liquid are mixed and covered with a greased cover-slip. A number of the mixtures are made, and the colour reaction with iodine is examined from time to time. The urease test with phenolphthalein can be carried out similarly.

J. W. M.

Physical Methods, Apparatus, etc.

Use of Camphor in Cryoscopy for the Determination of the Molecular Weight of Arsinic Acids. C. Schuster. (*J. Pharm. Chim.*, 1934, **19**, 497–498.)—Although the arsinic acids which are insoluble in the usual organic solvents are also insoluble in camphor (cryoscopic constant 500), the latter will dissolve derivatives similar in type to those formed by combination of compounds of arsinic oxides with thioglycollanilide (*cf. ibid.*, 1933, **17**, 28), and may, therefore, be used for the determination of molecular weights. The procedure is to heat a mixture of 0·1 to 0·33 grm. of the sample with 1·4 to 2·3 grms. of camphor in a test-tube immersed in an oil-bath until the mixture melts, and, during cooling, to determine the depression of the crystallisation point to within 0·25° C. on continuous stirring with the thermometer. The following results for 5 out of the 9 compounds tested show the experimental and theoretical molecular weights, respectively; the former are calculated from Raoult's law, and correspond with freezing-point depressions of from 5·75 to 21·5° C.:—*p*-Chlorophenyl arsenite thioglycollanilide, 520, 518; *m*-nitrophenyl arsenite thioglycollanilide, 520, 525, 529; diphenyl arsenite thioglycollanilide, 381·5, 388·5, 385; phenyl arsenite thioglycollanilide, 477, 472. J. G.

Application of Absorption Spectra in Oil Research. Distillation of Palm Oil. L. J. N. Van der Hulst. (*Rec. Trav. Chim. Pays-Bas,* **1934, 53,** 672.)—A comparison of the absorption spectra of palm oil and of a solution of carotene in bleached palm oil, and of their distillates and distillation residues, respectively, confirms the investigations of Waterman and Van Vlodrop (see p. 498). The measurements were made between wave-lengths 380 to 520$m\mu$ and in the absence of interfering substances. Distillation of a solution of carotene in colourless palm oil gave a concentration of carotene in the distillate with a very small amount in the residue, whilst with natural palm oil only a small increase of carotene in the distillate was found. If palm oil in hexane solution is bleached with about 100 per cent. of bleaching earth (Terrana "superior") an oil is left with a spectrum similar from 220 to 500$m\mu$ to that of a mixture of oleic and stearic acids.

D. G. H.

Reviews

THE ATOM. By JOHN TUTIN, D.Sc. With an Introduction by Prof. FREDERICK SODDY, F.R.S. London: Longmans Green & Co. 1934. Price 6s. net.

We have travelled far since the publication of the fateful paper which heralded the opening of a new century, and marked the close of that comfortable era when an atom was but an extremely minute billiard ball whose behaviour could be predicted by a straightforward application of those Newtonian laws of mechanics which have been deduced from the observation of the behaviour of molar masses. It is remarkable that these concepts of large-scale mechanics should bear such a staggering extrapolation; and simple and naïve as this mechanical atom may be, the notion is not without its value to-day. But the complexities of radio-active phenomena demand a more complex atomic model, and the nuclear atom was supplied by Rutherford and quantised by Bohr, in accordance with the views that had developed since the appearance of Planck's pioneer paper just mentioned.

So far, matters were perfectly precise, and the notion of the atom was clear-cut, even though it might be steadily increasing in complexity. But now the growth of wave mechanics has forced us to replace this definite structure of a minute, complex, massive nucleus with its accompanying planetary orbits of electrons by a *probability pattern* the density of which at any point gives us a measure of the chance of finding an electron there. Our concept has become a trifle hazy at the edges. None the less, it fulfils the pragmatic test—it works.

Dr. Tutin would change all this; he inverts the atom and has his light electrons as part of the nuclear structure, with the heavy masses in orbital motion. As he himself naïvely remarks by way of illustration: "It may seem at first sight difficult to accept the alternative of very heavy masses spinning round a very light nucleus, but from the purely mechanical point of view there is nothing impossible in such an arrangement. On the contrary, a flywheel with a heavy rim and a light hub is a far more commonplace conception than a flywheel with a light rim and a heavy hub."

The book is not without interest, but Dr. Tutin will have to delve far more deeply than he does into the intricacies of modern spectroscopy if he wishes his ingenious atom to be taken seriously.

A. FERGUSON

PHYSICO-CHEMICAL METHODS. By J. REILLY, M.A., D.Sc., Sc.D., and W. N. RAE, M.A., F.I.C. Second revised and enlarged edition. Pp. xv + 882. London: Methuen & Co., Ltd. 1933. Price 42s.

Physical measurements are becoming of increasing importance in chemical work, and this is true no less of analytical and industrial laboratories than of those in which research work is the primary objective. The up-to-date analyst must not only be familiar with the determination of viscosities, of refractive indices and of hydrogen ion concentrations, but he is now expected to study absorption, Raman and X-ray spectra, and even measure dielectric constants. Until the appearance, in 1926, of the first edition of the volume under review there was no text-book available in the English language—apart from the elementary books suitable for undergraduates—by means of which chemists could make themselves familiar with the general outlines of practical physico-chemical methods. A definite need for such a work has been clearly proved by the fact that a new edition has been called for, in spite of its high price, in such a comparatively short time after its initial publication.

The present edition contains seventy-five chapters, divided into the following nine sections: Introduction; The Physical-Chemistry Laboratory and its Equipment; General Operations; Physical Measurements; Some Molecular Properties; Some Properties of Gases and Vapours; Thermochemistry; Optical Measurements; and Electrical Properties. The reviewer has been able to think of very few important measurements in chemistry involving physical methods which do not find mention in the book, although the authors "make no claim to completeness on account of the wide scope of the subject." In a future edition mention might well be made of the "rotation" method in X-ray spectroscopy, of the corrections for the capillary tube diameter in surface tension measurements, of the modern developments in the "moving boundary" method of transport number determination, and of the polarograph.

It is true that a large number of subjects are mentioned in the book, but the extent to which they are treated varies very considerably, and this variation may not always be to the taste of the reader; for example, the section on distillation occupies nearly forty pages, but the infra-red spectrometer is dismissed in three lines. Such inequality seems inevitable when only two authors attempt a comprehensive work of this nature, and until the ideal treatise on physico-chemical methods, written by a dozen or more specialists, is available, the book under review can be warmly recommended to all chemists.

S. GLASSTONE

A TEXT-BOOK OF INORGANIC CHEMISTRY. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Volume VI, Part II: PHOSPHORUS. By EDMUND B. R. PRIDEAUX, M.A., B.Sc., D.Sc., F.I.C. Pp. xxviii+238. London: Charles Griffin & Co., Ltd. 1934. Price 18s. net.

This exhaustive monograph bears abundant evidence of diligent compilation, especially of the physico-chemical data; the text is interspersed with numerous tables relating to densities, vapour pressures, conductivities, surface tensions, dissociation pressures, specific heats and volumes, etc., of the phosphorus compounds. The text is subdivided into fifteen chapters, dealing with the element; its allotropy; the phosphides; compounds with hydrogen, the halogens, sulphur, nitrogen; oxy- and thiohalides; oxides, unsaturated oxyacids, and the phosphoric acids. The concluding chapter discusses phosphatic fertilisers.

The preface is a brief but lucid survey of the important position of the element in agriculture and technology (phosphate industry and match manufacture), and of the rôle which the study of its compounds has played in the development of pure chemistry. The reader of this scholarly treatise, with its wealth of references to original papers on every page, will no doubt regret that the groups of the Periodic System described in the earlier text-books of Dr. Friend's series have not been accorded the same detailed treatment as is followed in the more recent ones. The eight members of the fourth group—including such elements of cardinal importance as carbon and silicon, the latter being dismissed in 56 pages—have been dealt with in 468 pages of text, whilst the four volumes devoted to the fifth group will aggregate 900 to 1000 pages by the time the last volume, now in preparation, is published. It is to be hoped that new editions of some of the parts will be re-written and enlarged. The reviewer can testify from personal experience that the treatment of the platinum metals is hardly adequate for more advanced study.

W. R. SCHOELLER

A TEXT-BOOK OF ELEMENTARY QUALITATIVE ANALYSIS. By C. J. ENGELDER, Ph.D. Second Edition. Pp. viii+243. London: Chapman & Hall. 1933. Price 13s. 6d.

The first edition of this text-book was reviewed in this journal (ANALYST, 1930, 55, 417). In the preparation of the present one the author has taken the opportunity to make some re-arrangement and extension of the subject-matter. Thus, a section is devoted to the electro-chemical oxidation-reduction theory and the equilibria existing in the corresponding systems, whilst Part II, dealing with the detection and separation of the cations, has been re-written and enlarged, with decided advantage from the point of view of the student. Several minor improvements have been made, with the result that certain reactions have been more clearly described, and a few of the newer tests for some metals have been introduced.

A new and desirable feature is the treatment of the binding of the book by pyroxylin impregnation to render it waterproof. Tests made on the cover with strong acids and alkaline solutions showed that no permanent damage resulted after an exposure of ten minutes, although glacial acetic acid removed a little of the red colour. This immunity suggests that, judging from the condition of the text-books belonging to certain students after brief use, it would be advisable to submit the whole of the pages to this reagent-proofing treatment.

The care expended in the proof-reading of this book is reflected in the almost complete absence of errors, the only ones detected being the addition of a final "n" to "chromium" on p. 144, and on p. 9 a mis-numbered reference to Tables XIX and XX, which should be XVIII and XIX.

Little evidence of the American source of this volume is shown, except in the transatlantic spelling of the names of a few elements. The general excellence of the first edition is maintained in the present one, and the book is well worth the attention of all engaged in the teaching of analytical chemistry.

T. J. WARD

TECHNICAL GAS ANALYSIS. By GEORGE LUNGE, revised and rewritten by H. R. AMBLER, Ph.D. Pp. xvi+410, with 138 Figures and Diagrams. London: Gurney & Jackson, 33, Paternoster Row. 1934. Price 21s. net.

Twenty years ago the scientific public were fortunate in having so comprehensive a work upon gas analysis as that of Professor George Lunge. For many years it was the standard work upon the subject, and its very excellence is probably the reason why, despite the many advances in this science, it has not been challenged in its position of general supremacy. The revised edition, prepared by Dr. Ambler, must give general satisfaction, since it appears as an old friend, sufficiently up-to-date to satisfy the most modern of us and yet still in the old familiar form. The publishers and Dr. Ambler are to be congratulated upon having made so few alterations in the form and arrangement. They may even have gone too far in this direction by retaining the section upon gas analysis in acid and alkali manufacture. Chemical manufacture now covers a much wider field, and the special requirements of other industries might have been included.

The volume is divided mainly into general technique, volumetric methods, physical methods, methods for individual gas constituents and industrial applications.

The author rightly points out in the first place the importance of correct sampling. There are so many difficulties in obtaining a really representative sample that more space might well have been devoted to the procedure. Reliable methods of collecting average samples from both uniform and non-uniform seams should certainly have been fully described; at present references only are given.

The section on volumetric analysis deals first with the better-known types of apparatus, and then with the reagents necessary for the absorption of the different gaseous constituents. This is a comprehensive and useful section, and contains many references to literature where space does not permit of detailed description. The Bone and Wheeler apparatus is widely used in this country, and it is surprising that the author should illustrate on p. 70 the original form. The modified apparatus, which includes a copper oxide combustion tube and a reserve vessel for holding the residue for explosion, is much more useful. Fractional combustion of hydrogen and carbon monoxide is dealt with fairly fully, but would have been clearer if one apparatus had been shown in diagram. In the writer's experience many operators misuse the apparatus by employing unduly large volumes of reagent; the 5 ml. recommended by the author is much too large when one considers that the total volume of gas analysed is only from 10 to 20 ml.

The important question of the confining liquid in volumetric analysis is not dealt with fully. Mercury must generally be the recommended liquid, but there are occasions when water or certain solutions must be used. A table of solubilities of gas constituents in water, glycerin and water, calcium chloride solutions and certain reagents, would have been very useful, especially if related to a true factor.

The very considerable growth of physical methods is dealt with in a special section. Fractional distillation methods are well described; their importance has increased with the recent advances in the treatment of petroleum gas and in other catalytic processes.

Perhaps the most valuable section of the book is that dealing with special methods for the treatment of individual gases. The data given are conveniently cross-referenced to other sections of the book, and the information available is most comprehensive. There do not seem to be any omissions, although certain constituents could have been dealt with more fully than others. One of these is water vapour, the references regarding which are rather inadequate. Tables of equilibrium vapour pressures with the usual drying agents would have been helpful.

A volume such as this cannot deal adequately with so wide a subject as calorific value, but the principal methods of determining it are reviewed in a short section, and useful tables are provided for the calculation of calorific value from the results of analysis.

The use of devices for the automatic recording of the proportion of certain gaseous constituents is dealt with under flue gases, and a few of the proprietary apparatus are described. Such methods are so useful in the control of plant that this section might have been amplified by more complete descriptions and by the inclusion of methods for dealing with constituents other than those of flue gases. The Ranarex carbon dioxide recorder is little more than referred to, and the valuable Cambridge carbon dioxide and carbon monoxide recorder is not described at all.

The book is well printed in clear type and is freely illustrated. Both author and publisher are to be congratulated upon preserving the continuity of so old a friend as Lunge's Gas Analysis.

J. G. KING

THE DESIGN AND CONSTRUCTION OF HIGH-PRESSURE CHEMICAL PLANT. By HAROLD TONGUE. Pp. xi+420. London: Chapman & Hall. Price 30s.

Mr. Tongue's volume gives an excellent account of the technique of high-pressure chemistry as it is to-day. It is illustrated with a large number of excellent diagrams representing the high-pressure apparatus.

Since many chemical reactions involving gases take place with a decrease in volume, it is to be expected that the application of high pressures to gaseous reactions will be extended in the future. The working-out of a technique of high pressures was not alone sufficient to develop high-pressure chemistry. It was only the discovery of catalysts to enable the chemical reactions to take place under conditions in which the chemical equilibrium was over on the desired side, that caused the development of high-pressure chemistry. New catalysts are continually being discovered as they are required by the chemist and as high pressures are available to him.

The author devotes himself mostly to the science and practice of modern high-pressure methods, and gives only a short historical account of their development prior to 1910. He does not mention the first high-pressure laboratory in this country at Manchester, where Petavel and Hutton successfully installed plant in 1902 to work with gaseous pressures up to 200 atmospheres and temperatures up to those of the electric arc. There is no doubt that Haber used his knowledge of the work of Petavel and Hutton in first experimenting on the ammonia equilibrium at high pressures; and, later, Greenwood, who had learned this technique in Manchester, took it to Haber's laboratory and made accurate determinations of the ammonia equilibrium. The book can be recommended to all who may desire to use high pressures.

R. E. SLADE

Publications Received

A SUMMARY OF FOOD LAWS AND REGULATIONS. By C. L. HINTON. Pp. 90. London: The Nema Press Ltd. Price 21s. 0d.

THE NATURAL ORGANIC TANNINS. By M. NIERENSTEIN. Pp. 319. London: J. & A. Churchill Ltd. Price 21s. 0d.

ROAD MAKING AND ADMINISTRATION. By P. E. SPIELMANN and E. J. ELFORD. Pp. 441. London: Edward Arnold & Co. Price 25s. 0d. net.

AN ENQUIRY INTO THE NATURE OF CERTAIN NINETEENTH CENTURY PAMPHLETS. By J. CARTER and G. POLLARD. Pp. 400. London: Constable & Co. Ltd. Price 15s. 0d. net.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. REPORT OF THE ANNUAL MEETING, 1933.

THE ADSORPTION OF GASES BY SOLIDS. By S. J. GREGG. Pp. 120. London: Methuen & Co. Ltd. Price 2s. 6d. net.