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# THE ANALYST

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

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

### XVIII. A New Method for the Separation of Titanium from Zirconium and Hafnium.

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*(Work done under the Analytical Investigation Scheme.)*

*(Read at the Meeting, May 7, 1930.)*

The present position of the separation of titanium from zirconium (with hafnium) is as follows: precipitation of zirconium phosphate from solutions containing excess of sulphuric acid and hydrogen peroxide is the best-known method (Lundell and Knowles, Analyst, 1920, **45**, 28) capable of yielding accurate results, and eminently suitable for the detection and determination of minute amounts of zirconia, such as occur in rocks (Hillebrand). With increasing amounts of zirconia the method becomes distinctly less convenient. The voluminous slimy precipitate is difficult to filter, wash, and ignite to a white residue. This should not be weighed, since, apart from slight variations in its phosphoric acid content, it contains any hafnia that may be present; hence the necessity of fusing it with soda to eliminate phosphoric acid, and precipitating the oxides after another fusion with bisulphate. Occasionally the oxides still contain titania; this, as well as the difficulty of removing all of the phosphoric acid in one fusion, may render a repetition of the procedure necessary.

Another process similar to the preceding, and hence more attractive for subordinate amounts of zirconia, is that of Moser and Lessing (ANALYST, 1928, **53**, 458), based on the precipitation of zirconium arsenate from nitric acid solution containing hydrogen peroxide. In either process, the zirconia is precipitated first, and in combination with an acid radicle, which must be eliminated before the zirconia can be weighed. In Moser and Lessing's process this is done by solution of the ignited arsenate precipitate in strong sulphuric acid and distillation of the arsenic with hydrochloric acid and reducing agents; the zirconia is recovered from the residual liquor by double precipitation with ammonia. The results quoted are very satisfactory, but, from the manipulative point of view, a less complicated process would be desirable.

Our new tannin process, described below, should prove a welcome addition to the analyst's resources. We find it accurate, and the simplest of the procedures under discussion; as it leaves the zirconia in solution while precipitating the titania as a bulky coloured compound, it is best adapted for the separation of smaller quantities of titania from any amount of zirconia: hence it complements the two methods already discussed.

Before describing our method we shall have to deal with one other published procedure. This is Dittrich and Freund's process (*Z. anorg. Chem.*, 1908, **56**, 344), based on the formation of a soluble titanium complex of salicylic acid, zirconia remaining insoluble. A re-investigation of this method was undertaken because, so far as we know, it has never been commented upon in the literature.

RE-INVESTIGATION OF DITTRICH AND FREUND'S SALICYLATE METHOD.—The following is a brief outline of the separation procedure: The mixed oxides are fused with bisulphate, the sulphate solution precipitated with ammonia, and the washed precipitate dissolved in nitric acid. The clear nitrate solution, neutralised as nearly as possible, is poured, drop by drop, into a solution of ammonium salicylate (10 grms. in 50 c.c. water), maintained in a state of vigorous boiling. After half-an-hour's boiling the hot liquid (measuring 200 c.c.) is filtered; the precipitate $P^1$ is collected, well washed with hot 5 per cent. ammonium salicylate solution, ignited, and re-treated, if necessary. The titania in the filtrates, $F^1$ and $F^2$, is recovered by boiling with excess of ammonia.

Two experiments, in which the original directions were closely followed, gave results as under:

| | | Exp. 1. | | Exp. 2. | |
|---|---|---|---|---|---|
| | | $ZrO_2$. | $TiO_2$. | $ZrO_2$. | $TiO_2$. |
| | Taken (grms.) .. | 0·0536 | 0·1515 | 0·1513 | 0·0506 |
| Treatments: First | $P^1$, re-treated .. | 0·1234 | — | 0·1556 | — |
| | $F^1$ contained .. | 0·0014 | 0·0868 | 0·0055 | 0·0457 |
| Second | $P^2$ ,, .. | 0·0471 | 0·0075 | 0·1415 | 0·0032 |
| | $F^2$ ,, .. | 0·0080 | 0·0628 | 0·0053 | 0·0043 |
| | Recoveries .. | 0·0565 | 0·1571 | 0·1523 | 0·0532 |

It should be stated, in view of the positive recovery errors, that the purification of the final products from silica, iron, etc., was not attempted, our sole concern being the completeness of the separation. The precipitate, $P^2$, was fused with bisulphate, and the titania in the sulphate solution determined colorimetrically; the titania precipitates from $F^1$ and $F^2$ were tested for zirconia by the phosphate method (*vide supra*).

The low titania extraction in $F^1$, Exp. 1, was the result of an attempt at further neutralisation of the salicylate liquor during addition of the solution of the nitrates, a certain amount of salicylic acid having separated; in this treatment, part of the titanium complex was evidently decomposed, with precipitation of the titania; this probably accounts for the high titania content of $P^2$, *i.e.* 0·0075 grm. On the other hand, Exp. 2 proceeded quite normally, yet it resulted in incomplete extraction of the titania, 0·0032 grm. remaining insoluble after double treatment.

What surprised us more than the incomplete titanium extraction was the marked solubility of the zirconia in the salicylate solutions; no zirconia-free titanium fraction was obtained in the above and several other experiments. In one of these the final volume of the salicylate liquor, before filtration of the zirconium precipitate, was only 120 instead of 200 c.c., and the zirconia in $F^1$ was higher than before:

Exp. 3. Taken $ZrO_2$ 0·1013; $TiO_2$ 0·1059 grm.
$F^1$ contained ,, 0·0125; ,, 0·0799. $P^1$: 0·1189 grm.

We interpret the reaction as a hydrolytic dissociation of an unstable salicylic zirconyl complex more or less soluble in strong ammonium salicylate solution, but precipitated on dilution: in other words, a balanced or incomplete reaction akin to certain earth-acid precipitations such as tartaric hydrolysis (XVI, ANALYST, 1929, **54**, 708). Colloidal phenomena intervene in the precipitation, for some of the filtrates showed the Tyndall effect and had to be re-filtered after standing overnight. Reasoning by analogy, one would expect a precipitate of that nature to occlude a certain amount of the element which it is desired to obtain or keep in solution.

We are led to the conclusion that Dittrich and Freund's method is not strictly accurate. With small quantities of the two oxides the uncorrected results may represent a close approximation to the amounts actually present, owing to compensation of errors of opposite sign. For exact work, or substantial quantities of either oxide, however, the method should not be used without subsequent examination of the final products. Dittrich and Freund prescribe a silica correction for the titania fraction. We agree that this is indispensable; further, we find a test for iron to be necessary in the case of precipitates produced by ammonia.

It will be seen that Dittrich and Freund's process proved much more effective as a separation procedure than that of Noyes and Bray (*cf.* XV, ANALYST, 1929, **54**, 459). Nor is this surprising, seeing that the former start with a solution of the metals to be separated, whereas the latter attempt the extraction of a complex precipitate, and this with a solvent of relatively low salicylate concentration.

AUTHORS' TANNIN METHOD.—This method is simpler and quicker than those discussed; the double treatment required occupies about six hours. The tannin adsorption complex of titanium is of a vivid red colour, whilst the zirconium precipitate is whitish; this difference enables us to ascertain, not the co-precipitation of any zirconium with the titanium, but the completeness of the titanium precipitation. This is a great practical advantage, and recalls the salient features of our tannin methods for the separation of tantalum from niobium (IV, ANALYST, 1925, **50**, 486) and of the earth acids from zirconium (XIII, *id.*, 1928, **53**, 517). We have also shown that the tannin precipitation of titanium from oxalate or tartrate solution requires exact neutralisation (XI, *id.*, 1928, **53**, 265). Under such conditions zirconium and titanium are both quantitatively precipitated from tartrate solutions (XVII, *id.*, 1929, **54**, 710). In neutral oxalate solution, however, there is decided differential dissociation, titanyloxalates being less stable than zirconyloxalates. This is especially the case in the presence of a large amount of electrolyte; in a hot neutral solution half-saturated with respect to ammonium chloride, tannin causes immediate flocculation of the red titanium complex, but hardly any precipitation of zirconium, so that a repetition of the procedure results in the quantitative recovery of titania containing only traces of zirconia, if any. For the detection and determination of such traces, the phosphate method (*vide supra*) is most convenient.

If no ammonium chloride is added, only part of the titanium is precipitated, the rest remaining in red colloidal solution; a larger excess of tannin is required for flocculation, and this, in turn, causes undue precipitation of the zirconia.

Tannin adsorption complexes, in general, when properly precipitated, filter very well, and can always be collected on loose paper (Whatman No. 41). The precipitates being very bulky, the size of filters used in current analytical work limits their application to smaller quantities of oxides. Now we have for some time past applied suction filtration (using stronger filter paper and platinum cones) to our tannin precipitates, which thereby undergo marked reduction in volume. Thus, the tannin precipitate obtained from 0·1 grm. of titania can easily be collected and washed on an 11 cm. paper. Washing is best effected by returning the furrowed cake with the aid of a glass rod to the beaker, and pulping the clots with the wash-liquor.

THE SEPARATION.—The mixed oxides, containing an indefinite amount of zirconia but not much over 0·1 grm. of titania, are fused with bisulphate in a silica crucible, and the mass dissolved in a saturated solution of ammonium oxalate (3 grms.) in a 600 c.c. beaker, the bulk being kept below 150 c.c. The boiling solution is cautiously titrated with *N* ammonia to the appearance of a faint cloudiness, which is immediately removed with a minimum of *N* hydrochloric acid. After addition of an equal volume of saturated ammonium chloride solution (lime-free), the boiling is continued. The precipitant (a freshly-made, filtered 4 to 5 per cent. tannin solution) is now added, drop by drop, from a burette while the boiling liquid is being stirred; the amount of tannin should be about 12 times that

of the titania. The beaker is left on a hot plate, when the flocculent, red precipitate will gather into clouds, leaving the liquid clear. If the latter shows any orange-yellow tint, an insufficiency of tannin is indicated; further cautious addition of the reagent should be made to the boiling liquid as long as an orange precipitate is obtained. If, however, the clear liquid is colourless or of a pale straw-yellow tint, the titanium precipitation is probably complete. After a short digestion on the hot plate (less than one hour), the precipitate $P^1$ is collected under moderate suction (*vide supra*), washed with a solution of ammonium chloride and oxalate (5:1 per cent.), and ignited wet in a porcelain crucible.

The filtrate, $F^1$, is always tested for complete precipitation as follows: it is boiled, cautiously neutralised with $N$ ammonia, and treated, drop by drop, with the tannin solution until a slight precipitate is obtained. If this is dirty grey, the titanium precipitation is complete; if yellow to pale orange, titanium is still present, and must be collected into a further precipitate, $P^{1a}$, by addition of more tannin, etc., as described for $P^1$.

*Re-treatment of* $P^1$.—The ignited precipitate, $P^1$ or $P^1 + P^{1a}$, is weighed as a guide, fused with bisulphate, and the product dissolved in a saturated solution of 3 grms. of ammonium oxalate; the liquor is digested hot for a short time, and filtered for the removal of any minute particles of grit and calcium oxalate. The filtrate is submitted to the same procedure as before; this time, however, the quantity of tannin added is 12 times the weight of $P^1 + P^{1a}$. The precipitate, $P^2$, is again left to settle for a short time on the hot plate. After having been collected by suction filtration (the filtrate $F^2$ should always be tested for complete precipitation as $F^1$), washed, and ignited, it is weighed as $TiO_2$. If at all substantial, we submit it to lixiviation; it is transferred to a small beaker, cautiously moistened, and digested for half-an-hour with 10 to 20 c.c. of 0·5 $N$ hydrochloric acid on the water-bath, any lumps being broken up with a glass rod. The liquid is then rendered feebly ammoniacal, filtered, and the precipitate collected, washed, ignited, and weighed. The loss is usually of the order of 0·001 grm.

The freedom of the precipitate from zirconia may be ascertained by fusion with bisulphate, solution in 5 per cent. sulphuric acid, and addition of excess of hydrogen peroxide and di-ammonium phosphate. The smallest quantities of zirconia will be detected by the formation of a flocculent precipitate after standing overnight. The weight of the ignited precipitate, multiplied by 0·46, is subtracted from that of $P^2$ ignited after lixiviation.

Determination of the Zirconium.—The new method applies especially to oxide mixtures in which zirconia preponderates, and in such cases it may be taken by difference unless a more stringent test for the complete absence of titania is contemplated. For this, two methods are here given, of which we prefer the first.

(1) The combined filtrates, $F^{1+2}$ are boiled down with nitric (large excess) and sulphuric acids for the destruction of ammonium chloride, oxalate, and tannin; after cooling and diluting with water, the liquid (free from nitric acid) is neutralised

with sodium carbonate, filtered, and the filtrate hydrolysed by boiling with thio sulphate. The precipitated zirconia is collected, washed, ignited, and weighed, if desired; after fusion with bisulphate and solution in dilute sulphuric acid any titania present may be detected and determined with hydrogen peroxide.

(2) The filtrates $F^{1+2}$ are boiled with a moderate excess of ammonia, a little more tannin being added if the zirconium content is low. The discoloured precipitate is collected and washed with dilute ammonium nitrate solution, ignited, eached with 0·5 *N* hydrochloric acid, etc., as described for $P^2$, and weighed. The weight should be corrected for impurities, which are determined by fusion with bisulphate, solution in tartaric acid, and addition of ammonia, ammonium oxalate, and hydrogen sulphide water to the unfiltered solution. The small precipitate is ignited to $(SiO_2+Fe_2O_3+CaO)$.

RESULTS OF TEST ANALYSES.—In Exps. 7 to 12, the composition of the oxide mixture was not disclosed to the operator until he had performed the separation:

| | Taken (grms.). | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Exp. | $ZrO_2$ | $TiO_2$. | $P^1$. | $P^2$. | Error. | $P^3$ (*a*). | $ZrO_2$ in $F^3$ (*a*). | $ZrO_2$ found. |
| 4 | 0·2006 | 0·0210 | 0·0245 | 0·0214 | +0·0004 | 0·0213 | nil | 0·2012 (*d*) |
| 5 | 0·2073 | 0·0516 | 0·0572 | 0·0522 | +0·0006 | 0·0518 | (*b*) | 0·2063 (*d*) |
| 6 | 0·2001 | 0·0084 | 0·0092 | 0·0086 | +0·0002 | 0·0088 | nil | 0·1993 (*d*) |
| 7 | 0·2042 | 0·0316 | 0·0349 | 0·0325 | +0·0009 | (*c*) | nil | 0·2033 (*e*) |
| 8 | 0·1060 | 0·0438 | 0·0455 | 0·0446 | +0·0008 | (*c*) | (*b*) | 0·1052 (*e*) |
| 9 | 0·2096 | 0·0073 | 0·0092 | 0·0072 | −0·0001 | (*c*) | nil | 0·2097 (*e*) |
| 10 | 0·1532 | 0·0135 | 0·0142 | 0·0133 | −0·0002 | (*c*) | nil | 0·1534 (*e*) |
| 11 | 0·1221 | 0·0332 | 0·0470 | 0·0337 | +0·0005 | (*g*) | (*g*) | 0·1204 (*f*) |
| 12 | 0·1306 | 0·0538 | 0·0690 | 0·0534 | −0·0004 | (*g*) | (*g*) | 0·1295 (*f*) |

(*a*) In Exps. 4 to 10, $P^2$ was tested for purity by another repetition of the procedure, giving $P^3$, and $F^3$ which was tested for $ZrO_2$ by ammonia and tannin; in the two tests marked (*b*), a faint opalescence revealed traces of zirconia. (*c*) Not weighed. (*d*) By thiosulphate hydrolysis. (*e*) By difference; sum taken − $P^2$. (*f*) Purified ammonia precipitate. (*g*) See next paragraph.

In Exps. 11 and 12, $P^2$ was tested for zirconia by the phosphate method, and the recovered zirconia for titania by colorimetry:

| Exp. | $TiO_2$ Error. | $ZrO_2$ in $P^2$. | $TiO_2$ in recovered $ZrO_2$. |
|---|---|---|---|
| 11 | +0·0005 | 0·0006 | nil |
| 12 | −0·0004 | nil | 0·0006 |

In other words, the residual contamination of the two products, as detected and determined, closely corresponds with the observed titania errors. We submit that the new process, supplemented by these simple purity tests, is of a high order of analytical accuracy, and we are confident that it will be found more expeditious than the existing methods.

The procedure was applied in the analysis of samples of zircon-rutile sands from Travancore, which were treated according to our method for the analysis of Brazilian zirconium ore (ANALYST, 1919, **44**, 397). The ignited thiosulphate

hydrolysis precipitate, $RO_2$, from 0·5 grm. of mineral, was submitted to the tannin separation process, giving $P^1$ and $P^2$ (leached):

| Sample. | $RO_2$. | $P^1$. | $P^2$. | $TiO_2$ by other method. |
|---|---|---|---|---|
| A | 0·3379 | 0·0487 | 0·0437 | 0·0442 (*b*) |
| B | 0·3452 | 0·0742 | 0·0629 | 0·0625 (*b*) |
| C | 0·3223 | 0·0084 | 0·0062 | 0·0065 (*a*) |
| D | 0·3297 | 0·0212 | 0·0191 | 0·0188 (*a*) |
| E | 0·3532 | 0·1176 | 0·1152 | 0·1168 (*b*) |
| F | 0·3312 | 0·0149 | 0·0108 | 0·0110 (*a*) |

The results were checked in the following manner: In the case of the sands low in titania, marked (*a*), that constituent was also determined colorimetrically in aliquot parts of the solution obtained by fusion of the sand with bisulphate and solution in dilute sulphuric acid. The sands marked (*b*) were also fused with bisulphate, and the product dissolved in ammonium oxalate solution; the titania was then obtained by a single precipitation with tannin, the quantity of zirconia in the solutions not exceeding a few mgrms. This is due to the fact that zircon is refractory towards bisulphate, whereas rutile is readily attacked. Hence the great bulk of the zirconia was separated as an insoluble fusion residue, and not by the tannin method.

ANALYTICAL APPLICATION.—Having thus explained our new method, we now propose to show that it is capable of a more extended application to certain other elements or a group of elements. In the first place, it will be seen that the only essential difference between this new process and that for the separation of the earth acids from zirconia (XIII, *loc. cit.*) consists in the concentration of the ammonium chloride. We are satisfied, therefore, that the present process will also separate zirconia from the earth acids; in fact, it will be an improvement over the older process as regards separation of niobium from zirconium, as the niobium precipitate will flocculate more readily at the higher ammonium chloride concentration.

As a corollary, it follows that (subject to the limitation as to quantity, imposed by the bulk of the tannin precipitates), the new method supplies a means for the quantitative separation of zirconia from earth acids *plus* titania. An introductory discussion on the resolution of the ternary mixture ($M_2O_5+TiO_2+ZrO_2$) into its constituents formed the subject of Section XV (ANALYST, 1929, **54**, 453), in which a preliminary account was given of the quantitative possibilities of the new pyrosulphate and tannin method. The investigation of that method is in progress, but the quantitative results are as yet rather disappointing. The present procedure will enable us to attack a very difficult problem from a new angle.

Further, we have made preliminary experiments involving two other elements, namely, thorium and aluminium. In accordance with theoretical considerations, it was found that both elements behave like zirconium in not being precipitated by

tannin from neutralised oxalate solution containing ammonium chloride, a separation from titania being thus accomplished:

| Exp. | $TiO_2$ taken. | Added. | $P^1$ (leached). |
|---|---|---|---|
| 13 | 0·0479 | $ThO_2$ 0·1068 as nitrate | 0·0484 |
| 14 | 0·0532 | $Al_2O_3$ 0·2357 as alum | 0·0528 |

These observations lead to further interesting applications of our procedure, such as the separation of alumina from the earth acids, and thoria from the earth acids. These will be considered in due course.

Finally, it was shown in Section XVII (*loc. cit.*) that tantalum, niobium, titanium, zirconium, thorium, and aluminium are precipitated together by tannin from neutralised tartrate solution. This complex precipitate is expected to yield to the new method, furnishing a precipitate of earth acids and titania, and a soluble fraction composed of the remaining elements.

SUMMARY.—The present position of the titania-zirconia separation is reviewed, Dittrich and Freund's salicylate method being re-investigated. In our hands, the process did not lead to a clean-cut separation, the zirconia residue from a double treatment still containing titania, while some zirconia accompanied the titania into the filtrates. A new method is explained, based upon precipitation of the titania by tannin from a neutralised oxalate solution half-saturated with ammonium chloride; a repetition of the procedure results in the quantitative precipitation of the titania with only traces of zirconia, if any. The method is simpler and quicker than the published processes. A preliminary account is given of the extension of the new method to the separation of the earth acids or titania or both from any or all of the following: zirconia, thoria, and alumina.

PRELIMINARY NOTICE.—The precipitation of uranium by tannin from tartrate solution is under investigation; a brown flocculent precipitate is produced in the hot neutralised solution under the conditions recorded in Section XVII (*loc. cit.*). The quantitative course of the reaction is being studied.

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# New Adsorption Indicators for Argentometry, together with a Comparison of their Limits of Sensitiveness.

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A new type of indicator for silver nitrate titration work was introduced by Fajans in 1923. It was shown by Fajans and Hassel (*Z. Elektrochem.*, 1923, **29**, 495) and by Fajans and Wolf (*Z. anorg. Chem.*, 1924, **137**, 221) that fluorescein and certain substituted fluoresceins, such as eosin, could be used for determining the end-point when titrating soluble halides with silver nitrate. As the colour change with such dyestuffs takes place essentially upon the colloidally dispersed particles or upon the surface of the precipitate, they have come to be known as adsorption indicators. The value of Fajans' method has been confirmed by the experiments of Kolthoff and his collaborators (*Z. anal. Chem.*, 1927, **70**, 369; 1927, **71**, 235). More recently additions to the list of dyestuffs which can be used have been made by Pieters (*Chem. Weekblad*, 1929, **26**, 6) and by Kolthoff, Lauer and Sunde (*J. Amer. Chem. Soc.*, 1929, **51**, 3273).

The mode of action of such indicators is doubtless connected with a property which the silver halides have long been known to possess, *viz.*, the capacity for adsorbing either silver or halogen ions. This subject appears to have been first studied in a systematic manner by Lottermoser from 1905 onwards, who published a series of memoirs on the properties of silver iodide. It was shown that when dilute solutions of a soluble halide, such as potassium iodide, and silver nitrate were brought together, the charge on the hydrosol of silver iodide was positive in the presence of excess of silver ions, but negative when the halide ions were present in excess. When flocculation is effected, the precipitate adsorbs the corresponding ion (Lottermoser, Seifert, and Forstmann, *Kolloid Z.*, 1925, **36**, 230). If a dyestuff which is capable of ionising is present, what presumably happens is either:

$$AgX + \overset{+}{Ag}\ (\text{adsorbed}) + \text{Indicator } \overset{-}{\text{anion}} = AgX + \text{compound of Ag and indicator anion,}$$

or: $$AgX + \overset{-}{X}(\text{adsorbed}) + \text{Indicator } \overset{+}{\text{cation}} = AgX + \text{compound of indicator cation and halogen.}$$

Fajans explains the change of colour which takes place at the end-point in terms of deformation phenomena on the surface of the precipitate. Freundlich, however (*J. Chem. Soc.*, 1930, 173), adverting to Fajans' experiments, pointed out that it

was impossible to decide at present whether to attribute the change of colour to deformation of ions or to the production of an isomeric molecule.

## EXPERIMENTAL.

1. TITRATION OF FERROCYANIDES WITH SILVER NITRATE USING FLUORESCEIN.—Twenty c.c. of a solution of potassium ferrocyanide required 21·5 c.c. of a solution of silver nitrate containing 15·85 grms. of the salt per litre. The concentration of the solution was, therefore, 10·6 grms. of $K_4Fe(CN)_6 3H_2O$ per litre.

This result was checked by quantitative oxidation of the ferrocyanide solution by standard ceric sulphate in the manner described by Berry (ANALYST, 1929, **54**, 462). The solution of ceric sulphate was standardised with reference to its available oxygen and found to contain 0·932 grm. of available oxygen per litre.

Fifty c.c. of the ferrocyanide solution required 10·7 c.c. of ceric sulphate, from which it follows that the ferrocyanide solution contained 10·5 grms. of $K_4Fe(CN)_6 3H_2O$ per litre.

2. NEW INDICATORS FOR THE TITRATION OF HALIDES AND OF SILVER IN ACID SOLUTION.—As indicators of the fluorescein type must be used either in neutral or in very feebly acid solution, their applicability is necessarily somewhat restricted. According to Fajans and Wolf (*loc. cit.*), however, silver in acid solution of a concentration not exceeding 0·5 *N* can be titrated accurately with potassium bromide, with the use of rhodamine 6G as indicator. In view of the importance of finding more indicators available in acid solution, experiments were made with a number of dyestuffs, and it was found that chrysoidine and phosphine (Badische Anilin und Soda Fabrik) could be used for titrating acid solutions of silver nitrate with potassium bromide. With these indicators the precipitate of silver bromide remains colourless until the end-point is reached, when the dye is adsorbed by the precipitate, which assumes a salmon-pink colour. The use of these two dyestuffs was shortly abandoned, however, as it was found that much better results were obtained with *tartrazine*. When this indicator is used, the precipitate of silver chloride or bromide assumes a strong yellow colour as long as excess of silver ions are present in the solution. As soon as the end-point is reached by the addition of bromide ions, the colouring matter on the precipitate is released, and the supernatant liquid assumes a greenish yellow colour, the change being remarkably sharp. It was also found that a dyestuff described as *safranine* by the Badische Anilin und Soda Fabrik gave very good results when the titrations were carried out in the reverse direction (silver nitrate run into potassium bromide). This compound, which consists of glistening green crystals readily soluble in water to a dark red solution, is probably phenosafranine (see *Allen's Commercial Organic Analysis*, Vol. VI, p. 293). When a solution of a soluble chloride or bromide containing this indicator is titrated with silver nitrate, much of the red compound is adsorbed by the precipitate. At the end-point, the precipitate becomes suddenly

blue. Other specimens of safranine, consisting of dark red powders, were found to be useless.*

A considerable number of experiments were made, of which the following may be quoted by way of illustration:

(*a*) *Titration of* 0·1 *N Hydrochloric Acid.*—The solution was standardised by sodium dissolved in alcohol, and found to be 3·655 grms. of hydrogen chloride per litre. When titrated directly with a standard solution of silver nitrate, with safranine as indicator, the concentration of the acid was found to be 3·67 grms. per litre. Using the same solution of silver nitrate, and delivering the acid from the burette, tartrazine being used as indicator, a titration value of 3·67 grms. per litre was again obtained. The end-points with both indicators were found to be unaltered in the presence of a 0·5 *N* concentration of nitric acid; that with safranine, however, was appreciably less distinct.

(*b*) *Titration of a Solution of Lead Chloride.*—It was considered desirable to ascertain whether these two indicators were reliable in the presence of a heavy metal. A solution of lead chloride, containing 8·29 grms. of the salt per litre, when titrated directly with silver nitrate (safranine as indicator), gave a titration value of 8·30 grms. per litre. When excess of silver nitrate was added to the lead chloride solution, and the excess titrated with potassium bromide, using tartrazine as indicator, the result was 8·32 grms. of lead chloride per litre.

(*c*) *Applicability of Tartrazine in the Presence of Proteins.*—It may be added that the action of tartrazine is unaffected by the presence of fairly considerable quantities of protein matter. Solutions of sodium chloride containing varying quantities of colourless proteins, when analysed by adding excess of silver nitrate and titrating the excess with *N*/10 hydrochloric acid, were found to give reliable results. When the concentration of the protein is large, flocculation of the silver chloride is impeded in consequence of "protective colloid" action. In such cases, however, flocculation was readily effected by adding a divalent electrolyte, such as strontium nitrate.

The general applicability of the above methods in argentometry having been established, it became necessary to ascertain whether in a given titration a consistent end-point was indicated by a dyestuff, and also whether such an end-point coincided with the equivalent point. Experiments were, therefore, made with fluorescein, tartrazine, and safranine as indicators.

FLUORESCEIN.—Fifty c.c. of a silver nitrate solution, containing 31·6098 grms. of silver nitrate per litre, were taken for each titration. One hundred c.c. of a potassium bromide solution were run in from a pipette, and the titration was completed by adding a solution of potassium bromide of one-tenth of the original concentration. Parallel titrations were made, using for the determination of the

* Since the above was written, a specimen of phenosafranine, supplied by British Drug Houses, Ltd., has been found to give satisfactory results.

end-points (*a*) the colour change with fluorescein, and (*b*) the non-appearance of turbidity, with the following results :

| Indicator employed. | Volume of potassium bromide solution equivalent to 50 c.c. of silver nitrate. c.c. | Average discrepancy from mean. c.c. |
|---|---|---|
| Non-turbidity .. .. .. | 100·30 | |
| Do. .. .. .. .. | 100·20 | 0·025 |
| Do. .. .. .. .. | 100·25 | |
| Do. .. .. .. .. | 100·25 | |
| Fluorescein (3 drops of a 0·5 per cent. solution) | 100·10 | |
| Do. .. .. .. .. | 100·16 | 0·03 |
| Do. .. .. .. .. | 100·17 | |

TARTRAZINE.—As one of the authors was engaged in an investigation on silver cadmium alloys which involved numerous exact analyses, it was necessary to subject the tartrazine method to a critical examination under conditions as nearly identical as possible with those under which it was to be employed. For each titration a weighed quantity of highly purified silver, together with an approximately equal weight of highly purified cadmium, was dissolved in dilute nitric acid, and the nitrous acid expelled by boiling. Halogen-free potassium hydroxide solution was then added until a slight permanent precipitate of silver oxide was produced, followed by dilute sulphuric acid until the liquid became clear. Two sets of experiments were made. In both, the end-point, as determined by the non-appearance of turbidity, was taken as the equivalent point. In the first set, about 0·5 grm. of silver was taken in each experiment (the actual quantities varied between 0·4829 grm. and 0·5655 grm.), and the titrations were carried out against approximately $N/10$ potassium bromide. In the second set, quantities of silver, which varied between 1·0500 grm. and 1·0515 grm., were taken for each titration. Every titration was conducted by adding just less than the calculated quantity of approximately $N/10$ potassium bromide, followed by a solution of approximately $N/100$ potassium bromide. The potassium bromide solutions for the two sets of experiments were of slightly different concentrations.

*Set A.*—Each tartrazine titration was continued until the first appearance of a pale green colour in the supernatant liquid.

| Indicator employed. | Volume of potassium bromide solution equivalent to one grm. of silver. c.c. | Average discrepancy from mean. c.c. |
|---|---|---|
| Non-turbidity .. .. .. | 95·88 | |
| Do. .. .. .. | 95·92 | 0·02 |
| Do. .. .. .. | 95·88 | |
| Tartrazine (3 drops of a 0·5 per cent. solution) | 95·68 | |
| Do. .. .. .. | 95·66 | |
| Do. .. .. .. | 95·74 | 0·04 |
| Do. .. .. .. | 95·59 | |
| Do. .. .. .. | 95·61 | |
| Do. .. .. .. | 95·68 | |

*Set B.*—Each tartrazine titration was continued until the supernatant liquid acquired a rich yellowish green colour. The difference between the "pale green" end-point and the "rich green" end-point was very approximately 0·11 c.c. It will be noted from the results below that the difference between the non-turbidity end-point and the "rich green" end-point is 0·08 c.c.

| Indicator employed. | Volume of potassium bromide solution equivalent to one grm. of silver. c.c. | Average discrepancy from mean. c.c. |
|---|---|---|
| Non-turbidity .. .. .. | 95·48 | |
| Do. .. .. .. | 95·50 | 0·01 |
| Do. .. .. .. | 95·53 | |
| Tartrazine (4 drops of a 0·5 per cent. solution) | 95·40 | |
| Do. .. .. .. | 95·45 | 0·02 |
| Do. .. .. .. | 95·40 | |

SAFRANINE.—Equal weights of pure silver, varying between 1·0574 grm. and 1·0680 grm., and pure cadmium were dissolved in nitric acid, and the solutions partially neutralised as in the previous experiments. A measured excess of potassium bromide solution was added to each, and the solutions were titrated with standard silver nitrate (approximately $N/10$). This solution of silver nitrate was standardised with reference to potassium bromide, using safranine as indicator.

| Indicator employed. | Volume of potassium bromide solution equivalent to one grm. of silver. c.c. | Average discrepancy from mean. c.c. |
|---|---|---|
| Non-turbidity .. .. .. | 95·52 | |
| Do. .. .. .. | 95·50 | 0·007 |
| Do. .. .. .. | 95·50 | |
| Safranine (3 drops of a 0·25 per cent. solution) | 95·54 | |
| Do. .. .. .. | 95·29 | 0·09 |
| Do. .. .. .. | 95·37 | |

It will be observed that the end-points, as determined by the various dyestuffs, occur with about 0·1 c.c. less of the bromide solution than when the non-turbidity method is employed. Further, that the degree of variation among the end-points obtained with a dyestuff is greater than the corresponding variation with the non-appearance of turbidity. We regard tartrazine as being definitely preferable to safranine. The end-point with the former indicator should always be taken as the "rich-green" stage of the supernatant liquid, since the titration values so obtained approach extremely closely to those obtained by the non-appearance of turbidity. From the point of view of rapidity of working, the tartrazine method is decidedly preferable to the non-turbidity method, and numerous analyses of silver cadmium alloys have given ample proof of its value.

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# Further Work on the Refractometer in Milk Analysis.

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(*Read at the Meeting of the North of England Section, November* 30, 1929.)

In a previous paper (Analyst, 1927, **52**, 193) we have shown that the refraction of milk serum obtained by the use of copper sulphate solution varies to a considerable extent with the acidity of the sample, and that as the sample begins to develop acidity the refraction rises for a time and then falls. Although we did not deal at any length with the cause of this increase in refraction (the subsequent decrease is, of course, due to the decomposition of the lactose), we suggested that it might be due either to the effect of the acidity on the amount of proteins in solution in the serum, or to the fact that the amount of copper retained by the coagulum varies with the condition of the casein at the moment of adding the copper sulphate solution. One observation, however, which did not agree with either of these two suggestions was that the refraction of the copper sulphate serum of fresh milk appeared itself to increase on standing after it had been prepared.

Our subsequent work has made us realise that sufficient precautions were not taken in the earlier experiments to safeguard against concentration due to evaporation. Any such concentration would, of course, increase the refraction of the serum. As a result of experiments we have made we are now quite satisfied that the refraction of the copper sulphate serum of fresh milk does not increase, after the serum has once been prepared, in the course of a week or more, provided that adequate precautions are taken against evaporation. When the usual small beakers were allowed to stand under a bell jar along with an open dish of water, these increases were quite small as compared with previous increases noticed, and when a further series of experiments was carried out in which the sera were kept in small conical flasks tightly closed with rubber stoppers, there was no increase in refraction over a period of days, and therefore the increase formerly noticed need no longer be considered.

It has already been shown (*id.*, p. 208) that the amount of copper contained in the copper sulphate serum of a sour milk may be as much as twice that contained in the corresponding serum of the milk when fresh, and the increase in refraction which occurs, it would appear, is to be attributed largely, if not solely, to this cause.

When it became obvious that the increase in refraction of the copper sulphate serum which takes place as the milk becomes sour was due to the precipitation of a portion of the proteins prior to the addition of the copper sulphate solution by the acid formed in the milk, thus allowing more copper sulphate to pass into the serum,

it was decided to try other methods of precipitation to see whether other precipitants behaved in a similar manner. The results obtained by previous workers and by ourselves are contained in the following paragraphs:

(*a*) CALCIUM CHLORIDE SERUM.—The preparation of milk serum by the addition of calcium chloride solution has already been extensively considered, and it was not thought worth while to repeat work on which previous investigators seemed to be in agreement.

Thirty c.c. of milk are thoroughly mixed with 0·25 c.c. of a solution of calcium chloride (sp. gr. 1·1375) in a tube, which is then closed by a cork through which is passed a short piece of glass tubing to act as a condenser. The tube is heated in a boiling water bath for 15 minutes and then placed in cold water. Any water condensed in the tube is added, and the serum decanted.

(*b*) PHOSPHOTUNGSTIC ACID SERUM.—The preparation of a milk serum for refractometric purposes by the use of phosphotungstic acid does not appear to have been tried previously. The reagent used in our experiments was prepared by dissolving 7 grms. of phosphotungstic acid in water, adding 2·5 c.c. of hydrochloric acid, and diluting to 100 c.c. The refraction at 20° C. should be exactly 36·00, and, if necessary, water or strong hydrochloric acid should be added until this figure is exactly obtained. For the preparation of the serum 20 c.c. of milk are thoroughly shaken with 5 c.c. of the reagent and filtered through paper. A clear and bright serum is invariably obtained. The following results have been obtained by examining a series of milks from day to day. Twenty c.c. quantities of each milk were pipetted into tubes, and one precipitated each day with the phosphotungstic acid reagent (Temp. 15·5° to 17·0° C.).

TABLE I.

REFRACTION OF MILK ON STANDING (PHOSPHOTUNGSTIC ACID SERUM).

| | Age of milk in days. | | | | | |
|---|---|---|---|---|---|---|
| No. of milk. | 0. | 1. | 2. | 3. | 4. | 5. |
| 536 P.D. | 35·7 | 35·7 | 35·2 | 34·7 | 34·5 | 34·5 |
| 537 P.D. | 35·6 | 35·6 | 34·7 | 34·3 | 34·0 | 33·7 |
| 538 P.D. | 35·7 | 35·7 | 35·1 | 35·0 | 34·8 | 34·8 |
| 539 P.D. | 35·0 | 35·0 | 34·8 | 34·4 | 34·3 | 34·1 |
| 540 P.D. | 35·0 | 35·0 | 34·3 | 34·1 | 33·6 | 33·4 |
| 541 P.D. | 34·9 | 34·9 | 34·7 | 34·2 | 34·1 | 33·7 |

It will be observed that no increase in the refraction takes place, and that, in general, there is a considerable fall in the reading after the second day.

(*c*) DIALYSED IRON SERUM.—The application of Maclean's method to the preparation of milk serum was first suggested by H. Hurst (ANALYST, 1925, **50**, 438). A perfectly clear and bright serum can be obtained by thoroughly mixing equal quantities of milk and dialysed iron (B.D.H.) and filtering through paper. The disadvantage of the process is that it entails a considerable dilution of the milk. The great advantage, in addition to the ease of manipulation and the clarity of the filtrate, is the fact that the whole of the precipitant is removed along with the precipitate, leaving no foreign substance in the serum. The following

refractions were obtained on sera prepared from day to day from a milk, the acidity also being determined:

TABLE II.

REFRACTION OF MILK ON STANDING (DIALYSED IRON SERUM).

| | Age of milk in days. | | | | | |
|---|---|---|---|---|---|---|
| | 0. | 1. | 2. | 4. | 5. | 6. |
| Refraction | 26·3 | 26·25 | 26·15 | 25·6 | 25·6 | 25·5 |
| Acidity* | 1·9 | 1·95 | 4·8 | 10·1 | 10·0 | — |

* The number of c.c. of $N/10$ sodium hydroxide per 10 c.c. of milk, with phenolphthalein as indicator.

It will be observed that in this case also, as in that of phosphotungstic acid serum, no increase in the refraction accompanies souring.

(*d*) SOUR SERUM.—From a consideration of these results it was thought that the refraction of the serum obtained without the addition of any foreign material to the milk would be interesting, that is to say, the formation of a serum by the spontaneous curdling of the milk due to souring, a method which has been reported on favourably by previous workers, and which is an official process of the American A.O.A.C. It is carried out by allowing the milk to stand until the proteins have coagulated sufficiently for a clear serum to be obtained on filtration through paper. The great advantage of the method is, of course, that no foreign substance is added to the milk; the disadvantage is that the milk cannot be examined when fresh, and must be continually kept under observation until curdling takes place; moreover, the progress of souring cannot be controlled.

The serum was prepared from each of twenty milks as soon as they were sufficiently sour. The sera were kept in tightly stoppered flasks and the refraction observed from time to time. The results are set out in Table III below.

TABLE III.

REFRACTION OF MILK ON STANDING (SOUR SERUM. SEPARATE PORTIONS).

| | Age of milk in days. | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. of milk. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 12. | 16. | 20. |
| 1349 R.D. | — | 42·0 | 42·0 | — | 42·0 | 42·1 | 42·1 | 42·1 | 41·7 | — | 37·7 | — |
| 1350 R.D. | — | 42·0 | 42·0 | — | 42·0 | 42·0 | 41·4 | 40·3 | 39·0 | — | 32·1 | — |
| 1351 R.D. | — | 42·5 | 42·5 | — | 42·6 | 42·6 | 42·2 | 41·2 | 40·2 | — | 34·3 | — |
| 1354 R.D. | — | 41·8 | 42·0 | — | 42·0 | 42·0 | 41·2 | 40·3 | — | — | 33·4 | — |
| 1355 R.D. | — | 41·2 | 41·3 | — | 41·3 | 41·3 | 41·3 | 41·2 | 41·2 | — | 40·0 | — |
| 1356 R.D. | 42·7 | 42·6 | 42·7 | — | 42·7 | 42·7 | 42·7 | 42·6 | 42·5 | — | 41·7 | — |
| 1357 R.D. | 42·3 | 42·3 | 42·3 | — | 42·3 | 42·3 | 42·3 | 42·3 | 42·3 | — | 41·8 | — |
| 1358 R.D. | — | 41·3 | 41·3 | — | 41·3 | 41·3 | 41·3 | 41·2 | 41·2 | — | 40·5 | — |
| 1871 M.D. | — | — | — | 42·0 | 41·8 | 41·9 | 41·8 | 41·8 | 41·7 | 40·9 | — | 35·8 |
| 1872 M.D. | — | — | — | 41·7 | 41·7 | 41·7 | 41·5 | 41·5 | 41·5 | 41·3 | — | 40·7 |
| 1873 M.D. | — | — | — | 42·4 | 42·4 | 42·5 | 42·4 | 42·3 | 41·8 | 40·7 | — | 34·2 |
| 1874 M.D. | — | — | — | 41·2 | 41·2 | 41·2 | 41·1 | 41·1 | 41·1 | 40·7 | — | 38·8 |
| 1875 M.D. | — | 40·1 | — | 40·1 | 40·0 | 40·0 | 39·3 | 38·3 | 37·2 | 35·4 | — | 29·0 |
| 1876 M.D. | — | — | — | 39·9 | 39·8 | 39·9 | 39·8 | 39·7 | 39·2 | 38·4 | — | 36·4 |
| 1877 M.D. | — | — | — | 41·2 | 41·1 | 41·1 | 41·1 | 41·1 | 41·1 | 41·1 | — | 40·7 |
| 1878 M.D. | — | — | — | 42·1 | 42·1 | 42·1 | 42·1 | 42·0 | 41·8 | 40·8 | — | 36·6 |
| 1879 M.D. | — | — | — | 41·1 | 41·1 | 41·1 | 41·1 | 41·2 | 41·2 | 40·6 | — | 39·0 |
| 1880 M.D. | — | — | — | 39·8 | 39·8 | 39·8 | 39·7 | 39·5 | 39·0 | 37·6 | — | 32·5 |
| 1881 M.D. | — | — | — | 41·8 | 41·8 | 41·8 | 41·7 | 41·8 | 41·4 | 40·8 | — | 38·6 |
| 1882 M.D. | — | — | — | 41·7 | 41·7 | 41·7 | 41·7 | 41·7 | 41·4 | 40·5 | — | 34·9 |

In the second series of experiments the serum was not all prepared at once, but the milks were allowed to stand in tightly-corked bottles, and a small quantity was removed each day and filtered, the refractions of the filtered portions being determined. These are given in Table IV below.

TABLE IV.

REFRACTION OF MILK ON STANDING (SOUR SERUM) PORTIONS TAKEN FROM BULK.

| | Age of milk in days. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. of sample. | 3. | 4. | 5. | 6. | 7. | 8. | 10. | 11. | 13. | 17. |
| 1129 S.D. | — | 41·25 | 41·25 | 41·2 | 41·0 | 41·0 | 41·0 | 41·0 | 41·0 | 41·0 |
| 1130 S.D. | — | 41·15 | 41·15 | 41·2 | 41·0 | 41·0 | 40·95 | 40·9 | 40·9 | 40·6 |
| 1131 S.D. | 42·15 | 41·95 | 42·05 | 42·15 | 42·1 | 42·1 | 42·15 | 42·2 | 42·2 | 42·2 |
| 1132 S.D. | — | 41·95 | 41·85 | 41·85 | 41·8 | 41·75 | 41·8 | 41·8 | 41·8 | 41·6 |
| 1133 S.D. | 41·05 | 40·8 | 40·75 | 40·75 | 40·75 | 40·75 | 40·75 | 40·75 | 40·3 | 39·9 |
| 1134 S.D. | — | 40·75 | 40·6 | 40·55 | 40·5 | 40·3 | 40·25 | 40·2 | 39·9 | 39·35 |

It will be noticed that, as in the case of the phosphotungstic acid and the dialysed iron sera, no material increase in the refraction of the sour serum takes place on standing; in fact, for several days the readings are remarkably constant, and a steady fall then sets in. It is to be expected that the sera would not remain constant for so long if the milks were kept at a higher temperature. The milks and the sera in the above experiments (Tables III and IV) were kept at temperatures of 14·5° to 16·0° C.

## PART II.

### REFRACTIONS OF MILK SERA PREPARED IN DIFFERENT WAYS.

In the previous paper the average refraction given for copper sulphate serum from genuine fresh milk was 38·35. Similar work has been carried out with other methods of preparing sera. This is described below.

(1) PHOSPHOTUNGSTIC ACID.—In the discussion following the former paper (*loc. cit.*), Mr. E. R. Bolton, then President, made the suggestion that if the proteins were precipitated with phosphotungstic acid in all cases, a new series of figures would be obtained which might be of some value. This suggestion has been carried out, and 200 mixed milks taken from different parts of the County of Lancaster under the Food and Drugs Act, containing at least 8·5 per cent. of solids-not-fat, have had their refractions determined, both by the phosphotungstic acid and by the copper sulphate methods. The range for the readings of the phosphotungstic acid sera was 33·4–36·1, with an average of 34·9. One sample obtained from one cow gave a reading of 31·9. The difference between the reading of the copper

sulphate serum, and the phosphotungstic acid serum varied between 2·7 and 3·8, with an average of 3·25. The differences are set out in the following Table V.

TABLE V.

DIFFERENCES IN REFRACTION BETWEEN COPPER SULPHATE SERUM AND PHOSPHOTUNGSTIC ACID SERUM.

| Difference .. .. | 2·7 | 3·0 | 3·0 | 3·1 | 3·2 | 3·3 | 3·4 | 3·5 | 3·6 | 3·7 | 3·8 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. of samples .. | 1 | 1 | 16 | 40 | 40 | 52 | 24 | 15 | 3 | 4 | 2 |

It is possible that this difference is due to the albumin present in the milk being soluble in copper sulphate serum and insoluble in phosphotungstic acid serum, but we have not followed up this suggestion as a method of determining albumin, on account of the lack of an accurate gravimetric method for determining the actual amount of albumin present, as a check on the proposed process. If, as the result of work on milk proteins which is at present taking place elsewhere, an accurate and convenient gravimetric method for the determination of albumin is evolved, it seems quite likely that the study of this suggestion for the refractometric determination of albumin might well repay the trouble involved. It might also serve as a rapid and convenient method for the detection of heated milk, as, of course, the amount of albumin in heated milk is less than in fresh milk.

In the case of one milk, which had the smell and taste of heated milk, the difference found was only 2·2—a much smaller difference than that found in any of the fresh samples.

(2) DIALYSED IRON.—One hundred and ninety-nine samples, obtained from similar sources to those obtained for examination with phosphotungstic acid, were precipitated with dialysed iron. The refraction varied from 25·4 to 26·7, with an average of 26·1. By calculation it can be shown that this average is very near, arithmetically, to that obtained with other precipitants, after allowing for the extra dilution.

TABLE VI.

REFRACTION OF DIALYSED IRON SERUM.

| Refraction | 25·4 | 25·5 | 25·6 | 25·7 | 25·8 | 25·9 | 26·0 | 26·1 | 26·2 | 26·3 | 26·4 | 26·5 | 26·6 | 26·7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. of samples | 1 | 2 | 4 | 9 | 11 | 17 | 27 | 27 | 45 | 25 | 17 | 11 | 2 | 1 |

(3) SOUR SERUM.—Three hundred and fifty-one samples of milk, received in the ordinary way under the Food and Drugs Act, were examined each day and filtered as soon as good coagulation had taken place. The preliminary thickening was ignored, as it was found impossible to obtain a clear filtrate until coagulation was fairly complete. The range of refraction found was 39·6–44·1, with an average of 41·9. Three hundred and forty-four of these samples had a range of 40·6–43·3, with the same average.

It was considered not unlikely that the refraction obtained might vary to some extent with the conditions under which the souring takes place. A number of milks were, therefore, divided up into three or four portions of about 150 c.c. each and allowed to stand at different temperatures, the refraction of each portion being determined as soon as it was sufficiently sour to give a clear filtrate. The results obtained are set out in the following table:

TABLE VII.

REFRACTION OF MILK STANDING AT DIFFERENT TEMPERATURES TILL SOUR.

| No. of milk. | at 21° C. | | at 17° C. | | at 14° C. | | at 7° C. | |
|---|---|---|---|---|---|---|---|---|
| | Days. | Refraction. | Days. | Refraction. | Days. | Refraction. | Days. | Refraction. |
| P.D. 582 | 4 | 41·85 | 5 | 41·95 | | | 37 | 43·50 |
| P.D. 583 | 2 | 42·25 | 4 | 42·25 | | | 37 | 42·65 |
| P.D. 584 | 3 | 41·65 | 4 | 41·60 | | | 37 | 45·30 |
| P.D. 585 | 2 | 41·90 | 4 | 41·75 | | | 37 | 43·45 |
| P.D. 586 | 4 | 41·95 | 7 | 41·90 | | | 37 | 45·90 |
| P.D. 587 | 3 | 41·40 | 4 | 41·90 | | | 37 | 42·30 |
| S.D. 1209 | 3 | 41·30 | 4 | 41·25 | | | 24 | 43·00 |
| S.D. 1210 | 2 | 42·55 | 4 | 42·55 | | | 24 | 45·80 |
| S.D. 1211 | 2 | 40·10 | 3 | 40·15 | | | 12 | 40·40 |
| S.D. 1212 | 2 | 40·60 | 3 | 40·60 | | | 23 | 40·60 |
| S.D. 1213 | 2 | 40·60 | 3 | 40·60 | | | 18 | 41·80 |
| S.D. 1214 | 3 | 41·45 | 6 | 41·45 | | | 20 | 42·50 |
| P.D. 607 | 3 | 40·80 | 4 | 40·75 | 7 | 40·20 | 17 | 41·00 |
| P.D. 608 | 3 | 42·15 | 4 | 42·15 | 7 | 42·15 | 17 | 42·75 |
| P.D. 609 | 3 | 41·50 | 4 | 41·60 | 7 | 43·80 | 19 | 43·40 |
| P.D. 610 | 2 | 41·70 | 3 | 41·65 | 7 | 40·80 | 15 | 42·00 |
| P.D. 611 | 3 | 41·60 | 4 | 41·60 | 7 | 42·60 | 15 | 42·30 |
| P.D. 612 | 2 | 42·40 | 3 | 42·40 | 3 | 44·60 | 17 | 42·50 |

On looking at this table it will be observed that considerable differences in refraction may be obtained, and, further, that these differences are not uniform, although there is a distinct tendency for those sera which are obtained at the lower temperature to have the higher refraction. It would appear that in those cases where the refraction of the sour serum is to be made use of, the souring should take place at some fixed temperature. We would suggest a temperature of 21° C., which is that at which the cool incubator is usually kept, and which is fairly readily obtainable at all times of the year in most countries. From experiments which have been carried out it seems likely that the high results which are sometimes obtained at the lowest temperature used may be due to proteolysis. Thus, samples 584 P.D., 586 P.D., and 1210 S.D. contained, respectively, 0·26, 0·34, and 0·24 per cent. of nitrogen in the serum, whilst a milk which became sour at 16° C. contained 0·13 per cent. of nitrogen in the serum.

These figures are supported by the fact that those milks having higher refractions for their sour sera gave abnormally big precipitates with phosphotungstic acid, but precipitates of the normal size on coagulation of the albumin by heating.

In the following table the results are given of a number of milks which have been examined by all the methods suggested:

TABLE VIII.

REFRACTIONS OF MILK SERUM PREPARED IN DIFFERENT WAYS.

| | Dialysed iron. | Phosphotungstic acid. | Copper sulphate. | Spontaneous souring. |
|---|---|---|---|---|
| 1181 S.D. | 26·1 | 34·65 | 38·3 | 41·55 |
| 1182 S.D. | 26·15 | 34·75 | 38·2 | 42·0 |
| 1183 S.D. | 24·5 | 31·95 | 35·5 | 37·9 |
| 1184 S.D. | 25·85 | 34·7 | 37·9 | 41·75 |
| 1185 S.D. | 26·0 | 34·6 | 38·05 | 41·7 |
| 1186 S.D. | 26·2 | 35·15 | 38·4 | 42·15 |
| 924 O.D. | 26·1 | 35·15 | 38·55 | 42·9 |
| 926 O.D. | 26·0 | 25·05 | 38·35 | 41·75 |
| 928 O.D. | 26·0 | 34·9 | 38·25 | 42·0 |

(4) SERUM BY DIRECT FILTRATION.—It has been known for some time that it is possible to obtain a clear serum from fresh milk without the use of any precipitating agent whatever. This can be carried out by filtration of the milk through a Berkefeld filter candle or one of unglazed porcelain. The filtration is usually carried out by means of a good vacuum pump. We have given some attention to this method, on account of the great advantage that no foreign material need be added to the milk, but we find that, although the process is successful from the manipulative point of view, there are some disadvantages which weigh against its adoption for routine or even for frequent use. In the first place, a considerable time elapses from the beginning of the experiment until sufficient liquid is obtained for the determination of the refraction (usually standing overnight is necessary), and this may result in the serum not being quite fresh. Further, each milk requires a separate filter candle, and thus considerable labour is involved. Finally, and most serious of all, the refraction apparently varies according to the porosity of the filter. For instance, the same milk when filtered through a fine candle gave a serum having a refraction of 38·6, whilst that obtained in the case of a coarse candle was 40·5. The difference between these two figures may be due to the removal of albumin by the finer filter, but in any case would appear to be a serious, in fact, a fatal objection to the use of this particular method.

CONCLUSIONS.—As a result of our further work on this subject it would appear that the copper sulphate method for producing the serum is, on the whole, as useful as any that has been devised. It is true that it is necessary for the milk to be fresh, but the same objection, to a greater or less extent, applies to the other methods of precipitation by reagents which have been suggested. The phosphotungstic acid method has the advantage that no rise in the refraction occurs in the early stages of souring, but the removal of the albumin results in a lowering of the figure obtained, which may be a disadvantage. Where the sour serum method is used the souring should be carried out at a uniform temperature, and the refraction should be taken as soon after complete clotting as possible.

The following references to the use of the refractometer in milk analysis are supplementary to those given in our previous paper (*vide supra*).

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# The Gravimetric Determination of Aluminium, Chromium and Iron by means of Potassium Cyanate.

BY B. J. F. DORRINGTON, M.Sc., A.K.C., AND
A. M. WARD, B.Sc., Ph.D., A.I.C.

ALUMINIUM.—Ripan's method of determining aluminium by means of potassium cyanate (*Bul. Soc. Stiinte Cluj*, 1927, **3**, 311; *Chem. Zentrbl.*, 1927, ii, 2389) has given low and irregular results in our hands, and, contrary to Ripan's statement, the precipitate was gelatinous. Possible causes of this irregularity are: (*a*) Alumina may remain in solution owing to hydrolysis of the cyanate, possibly in accordance with the scheme—

$$4KCNO+6H_2O \longrightarrow 2K_2CO_3+(NH_4)_2CO_3+CO(NH_2)_2$$

(O. and I. Masson, *Z. physikal. Chem.*, 1910, **70**, 290); and (*b*) the use of water, instead of a solution of ammonium nitrate, for washing the precipitate.

We have attempted to eliminate these errors by means of a modified method in which the precipitate, after standing overnight, was washed with hot, faintly alkaline ammonium nitrate solution, then ignited in a platinum crucible, and finally heated for 2 hours in a muffle furnace, to convert the alumina into the insoluble and less hygroscopic variety.

The results were much more regular than those obtained by the original method, but the precipitate was not granular.

Precipitation of aluminium with potassium cyanate has not shown any advantage over the methods of Stock (*Ber.*, 1900, **33**, 548), Chancel, Wynkoop, or Schirm (*cf.* Treadwell and Hall, *Anal. Chem.*, 5th Ed., Vol. II, pp. 83–86).

DETERMINATION OF CHROMIUM.—The determination of chromium has also been described by Ripan (*Bul. Soc. Stiinte Cluj*, 1928, **4**, 57; *Chem. Zentrbl.*, 1928, i, 2973).

In fourteen determinations by Ripan's procedure ten results agreed well among themselves and with the ammonia precipitation results; and four of them were low. The same possible causes of discrepancy occur here as in his procedure for aluminium. In some determinations it was noted that a turbidity resulted when the final wash liquors fell into the main bulk of the filtrate, which would contain a higher concentration of electrolyte. This lends support to the view that some of the precipitate may be dissolved during the final washing with water. The method was, therefore, modified as follows:—

The chromium chloride solution (20 c.c.) was diluted to about 200 c.c. with cold water, ammonium chloride (5 grms.) and potassium cyanate (1 grm.) added, and the solution stirred until all had dissolved. The solution became of a deep green colour and no precipitate separated, but with a different batch of cyanate precipitation commenced at room temperature (with both specimens of cyanate, however, partial precipitation resulted on allowing the solutions to stand at room temperature overnight). The solution was slowly heated to about 70° C., when a fine granular precipitate began to separate; heating was slowly continued to boiling point, and, after standing, the turbid liquors were decanted through a Whatman filter (No. 41), and the precipitate washed once, by decantation, with ammonium nitrate solution (prepared by treating 20 c.c. of concentrated nitric acid with ammonia and diluting to 1 litre).

The filtrate was heated to boiling, alizarin S indicator added (Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 936), followed by hydrochloric acid until the solution was permanently yellow, and ammonia was then added until the indicator was just red. The solution was filtered through a separate filter, and the very small amount of precipitate washed with hot ammonium nitrate solution. The main bulk of the precipitate was washed by decantation with the same wash liquor, and then filtered off.

A film of precipitate adhered very firmly to the beaker, and could not be removed by continued washing. It was, therefore, dissolved in hydrochloric acid, and re-precipitated by ammonia in very slight excess, with alizarin S as indicator, and filtered off through the second filter. The precipitates were ignited wet in a platinum crucible.

The precipitates, after the filter paper was burnt off, were heated for 10 minutes over a large Meker burner; this heating suffices to bring the $Cr_2O_3$ to constant weight. The results were as follows:

| | | | |
|---|---|---|---|
| 0·1328 grm. | 0·1327 grm. | 0·1335 grm. | 0·1332 grm. |
| 0·1330 ,, | 0·1333 ,, | 0·1330 ,, | 0·1332 ,, |

The results obtained by precipitation from 10 c.c. of the solution by means of ammonia were :—0·0667 grm., 0·0665 grm. and 0·0667 grm.

DETERMINATION OF IRON.—The cyanate method has not previously been applied to this determination, but satisfactory results can be obtained by either of the following procedures: The precipitate is granular, and can be filtered off readily, although a film of precipitate adheres very firmly to the beaker; this must be removed as described in the determination of chromium. Main Smith vitreosil crucibles were used in all iron determinations, for the formation of $Fe_3O_4$ was not observed when using these crucibles, whereas, with platinum crucibles, reduction to $Fe_3O_4$ often took place (see T. B. Smith, *Analytical Processes*, 1929, p. 89).

(*a*) Ferric chloride solution (20 c.c.) was diluted to about 200 c.c., a few drops of concentrated hydrochloric acid added, and the solution heated to boiling. If the yellowish solution darkened during heating, sufficient concentrated hydrochloric acid was added to bring the solution back to its original colour; if the precipitation was carried out from a solution containing ferric hydroxide sol (as judged from the deep red-brown colour), the precipitate of ferric hydroxide was invariably bulky and gelatinous.

A concentrated aqueous solution of potassium cyanate (2 grms.) was added to the boiling solution as rapidly as possible, with vigorous stirring (the cyanate cannot be added all at once, otherwise frothing is excessive; but it is important that the ferric hydroxide sol stage should be passed through as quickly as possible). The solution was boiled for two to three minutes and the precipitate allowed to settle, well washed with hot water, filtered off, and ignited as in the determination of chromium. The results were as follows:

0·1854 grm. 0·1855 grm. 0·1856 grm. 0·1855 grm. 0·1855 grm.

The results obtained by precipitation from 10 c.c. of the solution by means of ammonia were:—0·0929 grm., 0·0929 grm.

(*b*) Twenty c.c. of the ferric chloride solution were diluted to about 200 c.c. with cold water, ammonium chloride (5 grms.) and potassium cyanate (1 grm.) added, and the solution stirred until the substances had dissolved. A precipitate slowly separated, and, after standing overnight, the clear supernatant liquors were decanted through a Whatman No. 41 filter paper, and the precipitate washed once by decantation with hot water. The procedure described under Chromium was then followed, except that Main Smith vitreosil crucibles (*Chem. News*, **1926**, **132**, 65), 7 cm. in diameter, were used, and that water was used for washing the precipitate.

The wet filters and precipitates were placed in the crucible, and heated at once from beneath with a full Bunsen flame, and then heated over a power-driven blowpipe until the carbon had burnt off. The crucible was at once re-heated for a further ten minutes over the blowpipe, cooled for twenty minutes in a desiccator, without the use of a drying agent, then left for fifteen minutes in the balance

case and weighed. The advantage of using these crucibles lies in the rapidity with which the filter papers may be burnt off, but their life is short, the glaze being soon destroyed in places, so that the exposed silica becomes very soft and flakes off easily.

The results obtained were as follows:

| | | | |
|---|---|---|---|
| 0·1697 grm. | 0·1698 grm. | 0·1690 grm. | 0·1701 grm. |
| 0·1698 ,, | 0·1701 ,, | 0·1702 ,, | 0·1698 ,, |

The determinations by precipitation from 10 c.c. of solution by means of ammonia gave the following results:

| | | | |
|---|---|---|---|
| 0·0850 grm. | 0·0851 grm. | 0·0849 grm. | 0·0854 grm. |

ZINC AND MANGANESE.—The methods for iron and chromium thus give precipitates which can be filtered off and washed much more readily than those obtained by the ammonia method of precipitation, but the application of a given method is governed to a considerable extent by its being peculiar to certain elements. The statement of Ripan (*Bul. Soc. Stiinte Cluj*, 1928, **4**, 57), that the presence of zinc and manganese ions does not interfere, would thus seem to render the method very valuable. More recently Moser and Siegmann (*Monatsh. Chem.*, 1930, **55**, 14; see ANALYST, 1930, **55**, 219) have applied the method to the determination of indium; they also consider methods for effecting the separation of indium from zinc, nickel, cobalt, and chromium by the cyanate method.

Our experiments showed that manganese is precipitated in considerable quantities by potassium cyanate in the presence of ammonium chloride, both on allowing the solution to stand at room temperature, and by boiling the solution. This result is apparently in accordance with Moser and Siegmann's observations. These authors state that if more than a tenfold excess of zinc over indium is present, the collected precipitate must be dissolved in dilute hydrochloric acid and precipitation repeated from the boiling solution. We found that zinc sulphate solution (prepared from zinc and sulphuric acid, both of A.R. quality), treated with ammonium chloride and potassium cyanate solutions under conditions comparable with those used in the above determinations, and allowed to stand overnight, gave a faint, but quite definite precipitate. If, however, the solution was boiled, only a small precipitate separated immediately, but, after boiling for a few minutes, a beautifully crystalline, white precipitate began to form, and boiling for half-an-hour sufficed to cause the separation of most of the zinc from the solution. The precipitate, which gave a copious evolution of carbon dioxide with acid, was presumably a zinc carbonate, formed by reaction with the potassium carbonate resulting from the hydrolysis of the potassium cyanate.

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# 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.*

## METHYLENE BLUE IN TINNED PEAS.

OWING to complaints from a number of consumers, a sample of tinned peas of Belgian origin was submitted for analysis. A paper label on the tin read as follows: "Green Peas. Liquor should be drained off on opening, and peas will get green within 3 minutes of exposure to air."

When the tin was first opened the peas were of a yellowish colour and became green on exposure to the air, as stated.

On analysis the sample was found to have been coloured with a blue basic dye having the characteristics of, and indistinguishable from, methylene blue. Methylene blue is listed in the United States as a harmful organic colour, and it is not included in the list of colouring matters permitted in foods. The use of methylene blue for colouring food is also prohibited in Switzerland. In England the Public Health (Preservatives, etc., in Food) Regulations, 1925 to 1927, prohibit the use of five coal tar colours, and, as methylene blue is not included in this number, the use of this colouring matter is permissible.

An interesting point is provided by the fact that the above Regulations prohibit the addition to food of metallic colouring matters which are compounds of certain metals. Methylene blue may occur commercially as a zinc double salt. If this salt had been used, the sample could be condemned. The method by which the dye, in whatever form, was originally introduced into the peas is not known to me, but an attempt was made by direct dyeing to simulate the green colour by boiling raw peas and water, in about the same proportion as found in the sample, with a solution of pure methylene blue; the hot liquid was then poured into a dish and the change of colour noted on exposure to air. It was found in this manner that when the mixture contained methylene blue in the proportion of one-twentieth grain per pound the blue colour penetrated inside the pea, and the liquid rapidly assumed a bluish shade. With one-fiftieth grain of methylene blue per pound, and with one-hundredth grain of methylene blue per pound, satisfactory greening effects were obtained by the method stated. (The medicinal dose of methylene blue is 1–4 grains.) The amount of zinc present in commercial methylene blue is approximately one-twelfth, so that the amount of zinc to be detected would be extremely small. The zinc found in the sample amounted to one-fifteenth grain per pound. Zinc, however, may be present in tinned peas naturally, and also accidentally, from the soldering flux. There is no reason to suppose that methylene blue (zinc-free) had not been used.

It would seem, therefore, that, as methylene blue is not a prohibited dye, and, as it is not possible to state whether or not it was originally combined with zinc, the only exception that can be taken to its use is that the presence of this dye is undesirable owing to the physiological effects, of which complaints were made.

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## CAP FOR HOLDING GUTZEIT MERCURIC CHLORIDE PAPERS.

SEVERAL devices for holding the mercuric chloride papers on the Gutzeit apparatus have already been described in this journal (ANALYST, 1927, **52**, 699, 700, 701; 1928, **53**, 152; 1930, 503), but the one depicted in the accompanying photograph is perhaps more readily constructed and used than the others, and has given complete satisfaction during the last 5 years.

The appliance consists of a loose-fitting cap which is dropped over the mercuric chloride paper, the latter resting on a flat-surfaced red rubber bung with one hole, which serves to close the upper end of the purifying tube.

The caps are constructed from pieces of glass, about 2 inches square, coarsely ground on the lower surface by rubbing on a large sheet of glass covered with water and sand of 20–30 mesh. The rims consist of rings cut from cardboard "former" tubes (used as axes for paper rolls, etc.) by means of a fine saw. The ground glass is heated on the floor of a boiling water oven, and a layer of sealing wax, marine glue, or, best of all, Chatterton's compound, is applied to one end of each ring; this is placed on the ground surface of the hot glass, and the whole is then allowed to cool, after which the cap is ready for use. After some months of daily use the ground surface of the glass in contact with the paper is liable to become stained, but the stain may be readily removed by warming, so as to soften the cement, removing the cardboard and regrinding the glass, as above described. Although these caps are light in weight (about 14 grms.), they are sufficiently heavy to prevent any passage of the evolved gases between the paper and the rubber stopper, so that, after traversing the paper, the escaping gas passes along the interstices of the ground glass surface, and uniformly coloured stains, with sharply defined edges, are produced.

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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.*

## CITY AND COUNTY OF KINGSTON-UPON-HULL.

### ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1929.

THE total number of samples examined was 1398, of which 1213 were analysed under the Food and Drugs Act, 739 being official samples, 474 informal samples, and 185 miscellaneous samples. The total number of adulterated samples was 55, while 16 were of suspicious character.

MILK.—Of the 605 samples examined, 560 were genuine. The reductase test was applied to 37 other samples, and 12 of these gave unsatisfactory results.

*"Dirt" in Milk.*—Of a total of 605 samples of milk received from the Sampling Officers under the Adulteration Acts, 14 contained unwarranted amounts of extraneous matters (dirt), a percentage of 2·3. The corresponding figure for the year 1928 was 1·0, the lowest recorded for some years. Seven of these 14 dirty samples were one-pint samples purchased and divided in the usual way, and they were found to contain appreciable amounts of dirt. The remaining 7 milks were the unsatisfactory samples of a total of 17 milks taken specially for examination for dirt; they were three-pint samples, allowing after division one pint for the determination of any extraneous matters. These seven samples were found to contain (1) 3·7 parts dirt (sand); (2) 2·5 parts (sand); (3) 2·2 parts (partly dung); (4) 4·9 parts (mainly dung); (5) 4·5 parts (partly dung); (6) 5·4 parts (mainly dung); and (7) 6·1 parts (mainly dung) in each 100,000 parts of the milk. The vendor of (1) was cautioned; samples (2) and (3) were reported as of suspicious character; and the two vendors of the remaining four samples (Nos. 4 to 7) were each fined £2 10s. by the Court.

The methods for the determination of dirt in milk continue to be the subject of investigation by a Committee of the Society of Public Analysts. The work has been protracted by initial difficulties, but these are in a fair way to solution, and it is expected that a satisfactory method of working will be evolved. When the task of this Committee is completed it is hoped that the Government will set up a standard of cleanliness for ordinary commercial milk.

CREAM.—One sample of bottled cream contained only 24 per cent. fat, and three "tinned" creams were also low in fat-content (23 to 25 per cent.). It is not desirable that such creams should be allowed to be sold in competition with fresh cream containing practically double the amount of fat, without a declaration on the label as to composition, but in the four cases mentioned only one (a tinned Danish cream) was so labelled. Moreover, it is highly objectionable that such statements as "Pure Thick Cream" should be permitted without qualification to describe cream containing no more than 25 per cent. of fat, for the public associates *thickness* in cream with *quality*. There is to-day, however, no necessary connection in these respects.

CHEESE.—The seven samples of soft cheese, wrapped in tin-foil, contained from 39 to 44 per cent. of water, and 25·5 to 32·5 per cent. of fat. They cost from 1s. 8½d. to 3s. 9½d. per lb., as compared with 1s. to 1s. 8d. per lb. for ordinary ripened hard cheese. All the samples comply with the requirements of the Cheese Bill before Parliament, *viz.* a minimum of 45 per cent. of fat on the dry substance.

"FRENCH" COFFEE.—Three samples of so-called "French" coffee were mixtures of coffee with 35, 50 and 50 per cent. of chicory. The description "French" as applied to a mixture of coffee and chicory, appears to be common in this country, though coffee in France is not usually a mixed article. The description is generally accompanied, as in these three samples, by the words: "A Mixture of Coffee and Chicory," in smaller type than the main title "French Coffee," and it is desirable that there should be some requirement as to the size of the lettering of the whole of the descriptive matter. There was such a requirement many years ago framed (by the Commissioners of Inland Revenue) to protect the revenue.

WHITE PEPPER COLOURED WITH TURMERIC.—Three samples were found to be true white pepper (pepper corns ground after removal of the outer husk) with the addition of a yellow colouring matter (turmeric). The practice of colouring pepper in this way is very objectionable. It masks the real colour of the pepper,

making it difficult to detect on cursory examination whether decortication has been properly done, and it gives an unsightly and unnatural yellow tinge to the pepper. The practice serves no good purpose, and is just another of those unwarranted interferences with our foodstuffs (albeit in this instance a minor one and concerning no more than a condiment) which it is difficult, in the present state of the law, to protest against successfully.

SUNLIGHT (ULTRA-VIOLET RAYS) OBSERVATIONS.—Records of ultra-violet light strength (units of fading of standard acetone and methylene blue solution) have been taken throughout the year at the central and suburban sites described in previous reports. Little variation is shown in the figures for these two stations, and observations at the suburban station were discontinued from the end of the year. In the following table the maximum and minimum daily averages recorded by various towns are given:

RECORDS OF ULTRA-VIOLET LIGHT.

| Place. | Units of fading. Daily average throughout the months mentioned. | |
|---|---|---|
| | Maximum. | Minimum. |
| Hull (Central) .. .. .. | 5·8 (June) | 0·1 (Jan.) |
| Hull (Suburban) .. .. | 6·0 (June) | 0·1 (Jan.) |
| Cardiff (Central) .. .. | 5·1 (June) | 0·5 (Dec.) |
| Cardiff (Suburban) .. .. | 5·0 (June) | 0·5 (Dec.) |
| Doncaster .. .. .. | 6·2 (Aug.) | 0·3 (Dec.) |
| Lowestoft .. .. .. | 11·7 (June) | 1·0 (Jan.) |
| London (Kingsway) .. .. | 3·8 (July) | 0·3 (Dec.) |
| London (Hampstead) .. .. | 5·4 (July) | 0·5 (Jan.) |
| Rochdale .. .. .. | 1·0 (July) | 0·03 (Dec.) |
| Stirling (Central) .. .. | 4·6 (June) | 0·4 (Dec.) |
| Stirling (Suburban) .. .. | 4·9 (June) | 0·4 (Dec.) |

ARNOLD R. TANKARD.

## JHARIA MINES BOARD OF HEALTH.

### ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1929.

FOUR hundred and eighty-five samples of foods, disinfectants and waters received from the Mining Settlements of the province of Bihar and Orissa were examined during the year.

GHEE.—Of 144 samples analysed, 61 were found adulterated or below the standard prescribed by the Bihar and Orissa Food Adulteration Act. The usual adulterant is the imported vegetable product sold as "vegetable ghee." In two cases the vendor professed to sell pure cow ghee, but each sample consisted wholly of mowah oil, the indigenous product largely used by the labouring population.

MUSTARD OIL.—This is extensively used in cooking by the labouring class. Of 173 samples analysed, 43 were found to be adulterated or below the standard. The usual adulterants found are linseed oil, niger seed oil (*Guizotia abyssinica*) and sesame oil.

TEA.—Of 13 samples analysed, 12 were found to be adulterated or not to conform to the prescribed standard. The principal fraudulent practices are the mixing of foreign dusts with tea dust and the sale of exhausted tea leaves.

MILK.—Of 40 samples analysed, 13 were found to contain added water.

B. K. MANDAL.

DHANBAN, BIHAR AND ORISSA.

# 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.*

## RANCID BUTTER.

ON July 31st a tradesman of Bethnal Green was summoned at Old Street Police Court for having sold butter which was certified by the Public Analyst, Mr. A. E. Parkes, to contain 8·5 per cent. excess of free fatty acids (10·52 per cent. in all), and was rancid.

The defendant stated that he made the butter himself for private consumption.

The Magistrate (Mr. Snell) imposed a fine of 1s. with 2 guineas costs.

## THE PURPORTED WEIGHT OF TEA.

ON August 14th a multiple-shop Company was summoned at Romford for selling, contrary to the Sale of Food (Weights and Measures) Act, tea in a wrapper which did not state the true minimum net weight.

Mr. C. Berridge, for the Essex County Council, said that the proceedings were taken under Sec. 4 of the Act, and the case depended upon the interpretation of the word "purport." If the particular packets purported to be less than two ounces they were exempt from the regulation, but his contention was that it was not obvious that the packets were less than two ounces.

An assistant inspector gave evidence as to the purchase of six packets, for which he paid a shilling. Three were broken open to ascertain the net weight of the tea, and the gross weights of the other packets were then ascertained. The net weights were 1 oz. $2\frac{1}{4}$ drms. to 1 oz. 3 drms., and the gross weights were 1 oz. $4\frac{3}{4}$ drms. to 1 oz. 5 drms. Other packets in the shop bore a statement of the net weight.

The solicitor for the defence contended that the defendants were exempt, because they sold packets which purported to be less than 2 ozs. It was clear from the weights mentioned by the inspector that this must have been obvious to the purchaser. A two-oz. packet was almost double the size of these twopenny packets.

The Bench were of opinion that there should have been some indication on the packets that they were under two ounces, and they therefore convicted, and fined the defendants 10s. in each of the three cases. They were prepared to state a case in the event of an appeal.

# Department of Scientific and Industrial Research.

## FOOD INVESTIGATION REPORT No. 38.

### WASTAGE IN IMPORTED FRUIT; ITS NATURE EXTENT, AND PREVENTION. J. BAKER.*

THE factors concerned in wastage of fruit may be due to fungal or physiological causes. Certain varieties of fruit are more susceptible to wastage than others, and time of picking, temperature of storage, delay between picking and shipment, and marketing and distribution of fruit may all involve contributory conditions.

APPLES.—The most important losses are caused by over-ripeness, fungal rotting, bitter pit and internal breakdown, freezing and development of scald; Jonathan spot and brown heart are also found. Bitter pit and internal breakdown are most common in certain varieties, but all varieties are liable to suffer from fungal rotting. A survey of the present knowledge with regard to each of these abnormalities is given, with suggested remedies, but it is emphasised that in many cases more work is required before marked improvement may be expected.

PEARS.—Over-ripeness is the main cause of wastage, but core breakdown, scald, abnormal ripening and fungal rotting are serious in certain varieties. Much wastage from the first cause would be prevented if control of temperature during transport could be improved, but some fruit is undoubtedly shipped too ripe.

PLUMS AND PEACHES.—These mostly suffer from over-ripeness and under-ripeness, and more adequate knowledge is required of the ripening process.

GRAPES.—Dropping (separation of berries from stalks) is the most common form of wastage, but the factors causing it are still obscure.

ORANGES.—The wastage in imported oranges is entirely due to fungal rotting, especially by *Penicillium italicum* and *P. digitatum*. Grape fruit suffers in a very similar way.

BANANAS.—Prevention of bruising is an important factor in preventing wastage, but lack of information of the effect of temperature on the banana prevents many improvements being suggested. The question is, however, being taken up by the Imperial College of Tropical Agriculture, Trinidad.

PINEAPPLES.—At certain times of the year the fungus, *Thielaviopsis paradoxa*, causes heavy losses in fruit from the Azores, but S. African varieties are liable to deteriorate after discharge from the ships, and this seems to be related to too low temperature of transport.

TOMATOES.—These suffer mostly from two types of fungal rot.

WASTAGE AND OVERSEA TRANSPORT.—Much wastage may be definitely attributed to imperfect control of temperature during transport, and the practice of keeping apples for long periods in store before shipment is also deprecated. Air circulation in the holds is very important, and the concentration of carbon dioxide should not rise over 5 per cent. Pre-cooling of all fruit shipped would certainly reduce wastage. Tentative optimal temperatures of transport are given as

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

follows:—For apples, 32 to 34° F., and 36–38° F. for New Zealand Jonathans; pears, 30–32° F.; peaches and plums, 32–34° F.; grapes, 32–34° F.; oranges and grape fruit, 40° F.; bananas, 54° F.; and pineapples, probably 45° F.

A survey of wastage during marketing is given, and time is regarded as a factor of primary importance. Rough handling during discharge and distribution is very destructive.

Although improvements in transport and marketing are very needful, yet the prevention of wastage must primarily be sought in the countries of growth of the fruits, and experimental work on such factors as humidity and concentration of carbon dioxide during storage and pre-storage is needed. The inter-relations of stock, strain, soil, cultural treatment, etc., need much working out.

D. G. H.

# Ministry of Agriculture.

## STATUTORY RULES AND ORDERS, 1930.*

### AGRICULTURAL PRODUCE (GRADING AND MARKING) (EGGS) REGULATIONS 1930.

In exercise of the powers conferred on him by the Agricultural Produce (Grading and Marking) Act, 1928, the Minister of Agriculture and Fisheries hereby makes the following regulations:—

1. Grade designations to indicate the quality of hen eggs produced in England and Wales shall be as follows:—

SPECIAL Weight. STANDARD Weight. MEDIUM Weight. PULLET Weight.

and the quality indicated by such grade designations shall be deemed to be as defined in columns (2) and (3) of the First Schedule hereto.

2. Grade designations to indicate the quality of duck eggs produced in England and Wales shall be as follows:—

SPECIAL Duck. STANDARD Duck. MEDIUM Duck. SMALL Duck.

and the quality indicated by such grade designations shall be deemed to be as defined in columns (2) and (3) of the Second Schedule hereto.

3. A grade designation mark shall be any one of the grade designations specified in regulations (1) and (2) above associated with the words "Empire Buying Begins at Home" and with the following mark, namely, a map of England and Wales in silhouette with the words "Produce of England and Wales" inscribed in a circle placed centrally in the map within which circle is a design representing the Union Jack, and which is more particularly described in the Third Schedule hereto.

4. After the twenty-eighth day of February, nineteen hundred and twenty-nine, any egg to which Section 3 of the aforesaid Act applies shall be marked conspicuously and legibly on the shell with the word "PRESERVED" in letters of not less than $\frac{1}{16}$ inch in height, the word being enclosed in a circle of not less than $\frac{1}{2}$ inch diameter.

5. If and so long as any Order in Council made under Section 2 of the Merchandise Marks Act, 1926, is in force prohibiting the sale or the exposure for sale in the United Kingdom of imported eggs unless they bear an indication of origin, any British egg which has been kept in cold storage or chemical storage shall, in the former case, be marked conspicuously and legibly on the

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

shell with the word "CHILLED" or with the words "COLD STORED" and, in the latter case, with the word "STERILISED," the letters being in each case not less than $\frac{1}{16}$ inch in height and the word or words being enclosed in a circle of not less than $\frac{1}{2}$ inch diameter.

6. When any person applies for the registration of premises to be used by way of trade or for purposes of gain for the cold storage or chemical storage of eggs, the Council of the County or County Borough, or, as respects the administrative County of London, the Common Council of the City of London and the Council of every Metropolitan Borough, in which the premises are situated shall enter in a register the name and address of the person and the address of the premises and shall forward a copy of each such entry to the Ministry of Agriculture and Fisheries and shall issue a certificate of registration to the person making the application.

7. These Regulations shall come into operation on the 10th March, 1930.

8. The Agricultural Produce (Grading and Marking) (Eggs) Regulations, 1928(*a*), shall be revoked as from the 24th March, 1930.

9. These Regulations may be cited as the Agricultural Produce (Grading and Marking) (Eggs) Regulations, 1930.

(*a*) S.R. & O. 1928, No. 984.

## SCHEDULE I.

HEN EGGS PRODUCED IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS OF QUALITY.

| Grade Designation. (1) | Definition of quality. | |
|---|---|---|
| | Minimum Weight. (2) | State or Condition. (3) |
| | oz. | |
| SPECIAL Weight .. .. | $2\frac{1}{4}$ | First Quality, *i.e.* the egg must not have been preserved by any process, the shell must be clean and sound, the yolk translucent or faintly but not clearly visible, the white translucent and firm and the air-space must not exceed $\frac{1}{4}$ inch in depth. |
| STANDARD Weight .. .. | 2 | |
| MEDIUM Weight .. .. | $1\frac{3}{4}$ | |
| PULLET Weight .. .. | $1\frac{1}{2}$ | |

## SCHEDULE II.

DUCK EGGS PRODUCED IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS OF QUALITY.

| Grade Designation. (1) | Definition of quality. | |
|---|---|---|
| | Minimum Weight. (2) | State or Condition. (3) |
| | oz. | |
| SPECIAL Duck .. .. .. | $2\frac{3}{4}$ | First Quality, *i.e.* the egg must not have been preserved by any process, the shell must be clean and sound, the yolk visible but not dense and moving slowly when the egg is rotated, and the white must not be translucent and firm. |
| STANDARD Duck .. .. | $2\frac{1}{2}$ | |
| MEDIUM Duck .. .. .. | $2\frac{1}{4}$ | |
| SMALL Duck .. .. .. | 2 | |

# United States Department of Agriculture.

## FOOD AND DRUG ADMINISTRATION.*

### REVISED AND AMENDED DEFINITIONS AND STANDARDS FOR FOOD-PRODUCTS. FRUIT JUICE AND WHEAT FLOUR.

THE following revised and amended definitions for food products are adopted:

1. Fruit juice is the clean, unfermented liquid obtained from the first pressing of sound, ripe, fresh fruit, or of its pulp, and conforms in name to the fruit from which it is obtained.

2. Grape juice is the clean, unfermented juice of sound, ripe grapes. It is obtained by a single pressing of the fruit, with or without the aid of heat, and with or without the removal of insoluble matter.

3. Orange juice is the clean, unfermented juice obtained from sound, ripe sweet oranges. It may contain a portion of the pulp and/or of the volatile oil.

4. Whole wheat flour, entire wheat flour, Graham flour, is the clean, sound product made by grinding wheat, and contains, in their natural proportions, all of the constituents of the cleaned grain.

7. Flour, wheat flour, white flour, is the clean, sound, fine-ground product, obtained in the commercial milling of wheat, and consists essentially of the starch and gluten of the endosperm. It contains not more than 15 per cent. of moisture, not less than 1 per cent. of nitrogen, not more than 1 per cent. of ash, and not more than 0·5 per cent. of fibre.

*Issued August*, 1930.

* *Service and Regulatory Announcements, Food and Drug No.* 2 (First Revision), Supplement No. 2.

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# ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

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# Food and Drugs Analysis.

**Occurrence of Crystalline Globulin in Banana Seeds. G. L. Keenan and J. D. Wildman.** (*J. Biol. Chem.*, 1930, **88**, 425–426.)—In the course of the examination of some banana seeds, large well-developed crystals of the octahedral type were observed in the starchy endosperm. They were found in the following varieties: Martini, Seminifera, Alis, Kacoloon, Bastard Hemp, Belox and Zampa, and were especially numerous in the seed of the Bola variety. The regular octahedra can be readily examined if the starchy endosperm is powdered and mounted in a suitable menstruum. The crystals vary in size from 15$\mu$ to 50$\mu$, with an average of 32$\mu$. Studies of the globulin from banana seeds have shown that its optical and microchemical properties are identical with those of the crystalline globulins isolated by Jones and Gersdorff (*J. Biol. Chem.*, 1923, **56**, 79; 1927, **75**, 213) from the squash and cantaloupe seeds. P. H. P.

**Identification of Flavouring Constituents of Commercial Flavours. J. B. Wilson and G. L. Keenan.** (*J. Assoc. Off. Agric. Chem.*, 1930, **13**, 389–397.)—The aldehydes and ketones of flavouring materials may be identified by examination of their semicarbazones. The semicarbazide solution is prepared by dissolving 11·2 grms. of the hydrochloride and 12·5 grms. of anhydrous sodium acetate in about 80 c.c. of hot water, filtering the solution into a 100 c.c. flask, washing the filter with hot water, and making the cold liquid up to the mark. A solution of 0·5 to 1 grm. of the aldehyde or ketone in 5–10 c.c. of alcohol is treated with 10 c.c. of the above reagent, 25–50 c.c. of water being added when crystallisation of the semicarbazide is well advanced. The crystals are filtered off on the following day and dried at 100° C. Smaller amounts of the materials may be treated, if necessary.

The semicarbazide is identified by means of its m.pt., its percentage nitrogen content (1 atom) determined by Veibel's method (ANALYST, **1928**, **53**, 53), the molecular weight calculated from this nitrogen content (N) by the formula, (1400·8 ÷ N) — 57·05, and the refractive indices along various crystal directions. These indices are measured by the immersion method, with the aid of a polarising microscope, the crystalline fragments being immersed in a series of mixtures of mineral oil ($n$ 1·49), monochloronaphthalene (1·64), monobromonaphthalene (1·66), and methylene iodide (1·74) with the difference 0·005 in refractive index between each mixture and its neighbour. Usually only the maximum and minimum refractive indices for any semicarbazone are necessary for its identification.

The following table gives, for a number of semicarbazones, (1) percentage of nitrogen (1 atom per molecule, as given by Veibel's method), (2) molecular weight, (3) m.pt., (4) $n_\alpha$, (5) $n_\beta$, (6) $n_\gamma$, and (7) the value of $n$ commonly observed:

| Semicarbazone | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Acetophenone | 7·91 | 120·0 | 197°C. | 1·480 | — | 1·660 | both |
| Anisaldehyde | 7·25 | 136·0 | 210 | 1·653 | 1·692 | 1·736 | 5 |
| Benzaldehyde | 8·59 | 106·0 | 217 | 1·560 | 1·685 | — | 5 |
| Benzylideneacetone | 6·89 | 146·0 | 186 | 1·450 | 1·618 | above 1·736 | both |
| Carvone | 6·76 | 150·1 | 143 | 1·490 | 1·645 | 1·710 | all |
| Citral | 6·70 | 152·1 | 132 | 1·560 | — | 1·660 | both |
| Ethylprotocatechualdehyde | 6·28 | 166·0 | 175 | 1·445 | (1·690) | above 1·736 | 5 |
| Heliotropin | 6·76 | 150·0 | 234 | 1·580 | — | 1·725 | both |
| *l*-Menthone | 6·63 | 154·1 | 184 | 1·528 | — | 1·590 | both |
| *p*-Methylacetophenone | 7·32 | 134·0 | 210 | 1·445 | — | 1·645 | both |
| Methyl undecyl ketone | 5·49 | 198·2 | 123 | 1·480 | 1·560 | 1·580 | 5 |
| β-Thujone | 6·70 | 153·1 | 170 | 1·520 | — | 1·590 | both |
| Vanillin | 6·70 | 152·0 | 230 | 1·692 | — | — | 4 |

Photomicrographs of some of the most characteristic of these semicarbazones are shown. T. H. P.

**Bio-assay of Capsicum. J. C. Munch.** (*J. Assoc. Off. Agric. Chem.*, 1930, **13**, 383–385.)—The U.S. Pharmacopeia specifies that a distinct sensation of pungency should be produced in the throats of at least two out of three individuals on swallowing 5 c.c. of a solution representing 14·3 mgrms. of crude capsicum or 2·86 mgrms. of oleoresin, extracted with 95 per cent. alcohol and diluted with

10 per cent. sucrose solution. Tests made on 94 individuals with a sample of capsaicin extracted from capsicum showed that, at the concentration 1:10,000,000, which has been reported as the threshold of detectable pungency, one-half of the tests gave positive and the remainder negative results. Capsaicin is not available in sufficient quantity to be used as a standard for evaluating individual sensitiveness to pungent substances, but piperine serves this purpose well, as solutions containing 0·015 grm. per litre gave no response, whereas those with 0·016 grm. showed definite pungency in the throats of ten individuals; three samples of piperine exhibited the same pungency. To determine the pungency of different samples of capsicum and of its oleoresin, the following procedure is recommended:—One grm. of the coarsely powdered capsicum is shaken with 50 c.c. of alcohol in a stoppered flask for 3 hours, and 0·1 c.c. of the clear supernatant liquor diluted with 100 c.c. of 10 per cent. sucrose solution. Five c.c. of this solution, swallowed during 5 seconds, should give the same sensation of pungency as is produced by 5 c.c. of 10 per cent. sucrose solution containing 0·016 mgrm. of piperine per litre. In case the latter solution is not satisfactorily pungent, the threshold concentration is determined and a corresponding alteration made in the standard for capsicum.

By this procedure the pungencies of a number of samples of capsicum and of its oleoresin have been determined, the minimum effective concentration varying from 20 to 400 mgrms. per litre for capsicums and from 3 to 20 for oleoresins. The method serves to distinguish between capsicum U.S.P. (medicinal) and the condiment varieties, which are essentially non-pungent, and to detect adulteration of commercial samples of capsicum and its oleoresin with such non-pungent forms.

T. H. P.

**Assay of Ipomoea. L. E. Warren.** (*J. Assoc. Off. Agric. Chem.*, **1930, 13,** 377–383.)—The following procedure is recommended for the determination of the resin in ipomoea: Ten grms. of the drug (as No. 60 powder) are heated for 30 minutes on a gently simmering steam bath, with occasional shaking, with 50 c.c. of alcohol in a 250 c.c. Erlenmeyer flask fitted with a glass reflux tube about two feet in length. The contents of the flask are transferred to a small percolator and treated with warm alcohol until about 95 c.c. of tincture are obtained. Completion of the extraction is judged by collecting a further 10 c.c. of percolate and pouring a few drops of this into water; only a faint cloudiness should appear. Any additional percolate is concentrated by evaporation and added to the original percolate, which is cooled and made up to 100 c.c. with alcohol. Twenty-five c.c. of the tincture are evaporated to dryness on a water-bath, and the residue dried until free from alcohol and then stirred well with 15 c.c. of boiling water to ensure thorough washing of the resin. The vessel is cooled by immersion in cold water, and the wash water decanted on to a 9 cm. filter paper. The resin is washed with another 15 c.c. portion of boiling water, the mixture being cooled after kneading the resin, and the washings decanted on to the filter. If the second wash water is more than slightly coloured, it is advisable to wash the resin a third time with boiling water. The residue in the containing vessel is dissolved in 15 c.c. of warm alcohol, and the solution poured on to the filter, the filtrate being collected

in a tared beaker. Sufficient hot alcohol in small portions is used to transfer the solution of the resin completely to the filter and to wash the filter thoroughly. The combined filtrate and washings are evaporated, the container being rotated in an inclined position as the last portions of the solvent are dissipated. The residue is dried at 100° C. to constant weight. T. H. P.

**Detection in the Urine of some Drugs used in the Treatment of Malaria. R. Green.** (*Ind. Med. Gaz.*, 1929, **64**.)—*A. Detection of some of the Alkaloids of Cinchona.*—With quinine, euquinine and cinchonine no reaction with Mayer's reagent was obtained with the urine until 2 hours after administration, but with quinine sulphate a reaction was obtained after 40 minutes, 1 hour, and 2 hours; with quinine hydrochloride in one case in 20 minutes, and in two cases in 40 minutes. With quinine alkaloid maximum excretion appeared to be between the third and the eighth hours; and with quinine sulphate, between the third and ninth hours; with quinine hydrochloride and euquinine, the second and fifth; and with cinchonine, between the second and seventh hours. The drugs ceased to be demonstrable between the ninth to thirteenth hours. A chart showing results is given.

*B. Detection of Plasmoquine in the Urine.*—The detection of plasmoquine in the urine (described by Schulemann, Schönnöfer and Wingler, 1927) is carried out by mixing 200–300 c.c. of urine with 20 c.c. of 50 per cent. potassium hydroxide solution, extracting the freed base with ether, rapidly filtering the extract (90 c.c.), and washing twice with 10 c.c. of water containing 2 drops of *N* sodium hydroxide. The plasmoquine is then extracted from the ether by shaking with 6 c.c. of 2 per cent. acetic acid, the acid separated, warmed, and to 3 c.c. of acid is added about 0·05 grm. of chloranil, and the mixture warmed for 90 seconds; if more than one part of plasmoquine in 50,000 is present, a blue or blue green colour develops. On cooling, excess of chloranil crystallises out, and, after filtering, 1 to 1·5 c.c. of ether are added to the filtrate, the ether remaining in solution until the acetic acid is partly neutralised by addition of a few drops of 50 per cent. potassium hydroxide, when it separates as a deep blue layer if plasmoquine is present. A few drops of alcohol hasten and render more complete the separation of the ethereal layer, and a preliminary chilling of the urine was found beneficial. The test, said to be effective with 100 c.c. of urine containing 1:2,000,000 of plasmoquine, could not be used to indicate the period of absorption and maximum excretion of plasmoquinine, as the quantity present was insufficient, but positive results were obtained in three cases in the total amounts of urine passed in the first eight-hour period after administration of 0·03 grm., and negative results in the two subsequent periods. D. G. H.

# Biochemical.

**Determination of Manganese in Animal Materials. J. T. Skinner and W. H. Peterson.** (*J. Biol. Chem.*, 1930, **88**, 347–351.)—In a study of the

manganese metabolism of rats it became necessary to analyse the material from many animals for its manganese content. Serious interference, due to the precipitation of calcium sulphate, was encountered when the official periodate method was applied to these samples. While attempts were being made to overcome this interference Davidson and Capen (*J. Assoc. Off. Agric. Chemists*, 1929, **12**, 310) gave a modification of the official method in which hydrochloric acid is replaced by nitric, sulphuric, or phosphoric acid, thus shortening the method and giving as good or better results. When phosphoric acid was tried in the analysis of the animal materials, the interference of calcium salts was almost entirely overcome. The periodate method has, therefore, been adapted to the determination of the small quantities of manganese found in animal tissue, and without the necessity for the use of a large and unwieldy weight of sample (10 to 20 grms. of the sample are sufficient). As little as 0·01 mgrm. of manganese has been satisfactorily determined. The analysis of bone is the most difficult and tedious determination to which the method has been applied. Good recoveries of added manganese were obtained, regardless of whether the manganese was added before or after the ashing. The method is applicable to a wide variety of animal materials; this is shown by data obtained in the analysis of ten representative foodstuffs. Although the actual amount of manganese in the samples ranged from 0·0062 to 0·0315 mgrm., recoveries which ranged from 88·5 to 104·5 per cent. were obtained. P. H. P.

**Determination of Bromides in Biological Material. L. D. Behr, J. W. Palmer and H. T. Clarke.** (*J. Biol. Chem.*, 1930, **88**, 131–135.)—A simple and moderately accurate method is described for the determination of bromides in biological fluids. The determination of bromides in the presence of relatively large amounts of chlorides is a problem which has attracted much attention. The new method is based on the fact that bromides can be almost selectively oxidised by permanganate in dilute phosphoric acid, and that the resulting bromine can be quantitatively transferred to carbon tetrachloride. In the presence of much chloride a small proportion of chlorine is also taken up by the carbon tetrachloride; the separation can, however, be made practically complete by the reduction of the liberated halogens with sodium sulphite and the repeating of the process two or three times. Under the conditions adopted, any iodide which may originally have been present is oxidised to iodate and thus escapes extraction by the organic solvent. Removal of the organic matter from the original sample is necessary, and involves an ashing process. No appreciable loss of bromide occurs when the incineration is conducted in platinum vessels at a temperature of 460 to 475° C., in the presence of potassium hydroxide. The extracts from the third oxidation are added to potassium iodide solution, and the liberated iodine is titrated with 0·01 *N* thiosulphate. Full details of the method are given, and tables show the recovery of bromine with the method when two reduction stages were employed. Two composite samples of human blood were analysed, with and without the addition of sodium bromide; results show the loss to be within the error of the analytical procedure. P. H. P.

**Determination of Blood Urea Nitrogen by Direct Nesslerisation. J. M. Looney.** (*J. Biol. Chem.*, 1930, **88**, 189–195.)—The determination of urea nitrogen in blood filtrates is a most troublesome procedure, and attempts to overcome the difficulties by direct Nesslerisation have been made. A direct Nesslerisation method would be of great value if the formation of turbid solutions could be prevented. The author has found that gum ghatti will act as a protective colloid; with distilled water, 1 c.c. of 2 per cent. gum ghatti will permit the Nesslerisation of solutions containing as much as 2·5 mgrms. of nitrogen in 100 c.c., without the appearance of turbidity for several hours. By the use of more of the gum even greater concentrations of ammonium salts can be kept clear. When tap water is used to make up the solutions, as much as 1 mgrm. of ammonium nitrogen per 100 c.c. can be Nesslerised without any trace of turbidity when the gum is used. The standard must contain the same concentration of gum ghatti as the unknown, because the presence of the gum decreases the intensity of the colour about 10 per cent.; this decrease in the intensity does not affect the accuracy of the method. The presence of urease also causes a slight decrease in the intensity of the colour, and for this reason the standard must contain the same concentration of enzyme as the filtrate. It is shown that urea added to blood filtrate is recovered by this method with a maximum loss of only 2 per cent. The figures obtained by the method are shown to agree very well with the results obtained on the same filtrates by aeration or distillation. When urease was not added to a standard, the average loss was about 3 per cent., which is also the figure obtained when a urease-containing standard was read against a non-urease-containing standard. Figures obtained seem to indicate that the aeration method as used in routine work gives results that are about 3 per cent. too low. For clinical work this error is negligible, and would indicate that the addition of urease to the standard is a refinement that is not absolutely necessary. P. H. P.

**Presence of Acetylmethylcarbinol and of 2:3-Butylene-glycol in the Blood of the Higher Animals. M. Lemoigne and P. Monguillon.** (*Comptes rend.*, 1930, **191**, 80–83.)—The presence of acetylmethylcarbinol and of 2:3-butyleneglycol was noted in the blood of the ox, sheep, pig, and horse, and, since it had previously been ascertained to be present in plants and in many unicellular organisms, the substances are regarded as important physiological products. The blood is coagulated by means of ferric chloride, and the coagulate distilled in a current of steam. The distillate is rectified, and the diacetyl from the acetylmethylcarbinol determined as nickel dimethylglyoxime. The undistilled residue is heated with bromine and again subjected to a current of steam and rectified, and may then be used for the determination of the diacetyl derived from the oxidation of the 2:3-butyleneglycol. Glucosides, lipoids, proteins, and complex mixtures did not give diacetyl under the above conditions. Confirmation was obtained by finding acetylmethylcarbinol in the distillate from the blood.

D. G. H.

**Further Observations on the Relation of Carotene to Vitamin *A*. J. C. Drummond, B. Ahmad and R. A. Morton.** (*J. Soc. Chem. Ind.*, 1930, **49**, 291–296T.)—The observation that carotene will not serve as a source of vitamin *A* for growing rats (ANALYST, 1929, **54**, 764) is found to be erroneous, since the solvent used, namely, ethyl oleate, has been found to undergo oxidation rather readily when purified. Ethyl laurate, prepared from the unsaponifiable constituents, and giving no iodine value, is recommended as a solvent, and the smallest dose of pure carotene to produce an appreciable gain in weight in young rats appears to be about 0·005 mgrm. daily. The claim of Euler, that dihydro-α-crocetin may replace vitamin *A* in the diet, is not confirmed. Palm oils, owing to their carotene content, are regarded as valuable sources of vitamin *A* for animals, one sample investigated being found equal in value to a good medicinal cod-liver oil. There is no question of the identity of carotene with vitamin *A* (ANALYST, 1929, **54**, 764), and there is evidence that the vitamin is a colourless substance. It seems probable that there is a conversion in the animal tissues of the pigment into a substance possessing the characteristics that for some time have been ascribed to vitamin *A*, and the observation that the unsaponifiable fraction of butter may contain both carotene and vitamin *A*, is regarded as of interest (Morton and Heilbron, *J. Soc. Chem. Ind.*, 1930, **49**, 238). The inter-relation of the vitamin and carotene may facilitate the quantitative determination of the former, since the determination of carotene should be simple, and a method of assay of vitamin *A*, based on the measurement of the intensity of the natural band at 328$\mu\mu$, and of the bands at 624 or 605$\mu\mu$ (produced on reaction with antimony chloride), appears more promising than the present crude biological method. Visual measurement will be insufficient, since dihydroergosterol, for example, would give a very similar colour. D. G. H.

**Vitamins in Dried Fruits. II. Effect of Drying and of Sulphur Dioxide upon Vitamin *A* Content of Fruits. A. F. Morgan and A. Field.** (*J. Biol. Chem.*, 1930, **88**, 9–25.)—The remarkably protective effect of sulphur dioxide upon the vitamin *C* of dried peaches was reported by the authors (*J. Biol. Chem.*, 1929, **82**, 579; ANALYST, 1929, **54**, 483), and its effect has now been studied on the vitamin *A* of fruits. The vitamin *A* content of frozen fresh and variously dried samples of peaches, prunes and apricots was determined by uniform biological technique. The sulphured dehydrated fruit in all cases appeared to retain the largest proportion of the vitamin; this retention was not directly related to the amount of sulphur dioxide in the fruit. Of the unsulphured fruit, the sun-dried specimens of prunes and peaches showed better retention of vitamin *A* than did the corresponding unsulphured dehydrated products. Lye dipping of the dried prunes had no apparent effect upon vitamin *A* retention. The amount of destruction of vitamin *A*, produced by comparable methods of preservation, varies widely in the three fruits. The vitamin *A* of peaches is little affected by any of the drying processes; 86 to 100 per cent. are retained in all cases. For prunes, however, 24 to 91 per cent. are retained, and for apricots only 16 to 51 per cent. of the fresh

fruit value are present in the dried preparations. The dried apricots which had lost the greatest proportion of their fresh fruit vitamin *A* content were still absolutely richer in this vitamin than the best of the peach and prune products. Storage of both sulphured and unsulphured apricots and prunes at 0° C. for a period of more than a year brought about no detectable loss of vitamin *A* content. The vitamin *A* content of two varieties of yellow peaches, of prunes, and of apricots is shown to be relatively large; that of the apricots compares favourably with the best figures reported for spinach, egg yolk or butter. The peaches and prunes had less vitamin *A* than the apricots, but as much or more than tomatoes, bananas or lettuce. The conditions which favour retention of both vitamins *A* and *C* in dried fruit products do not meet with popular or official approval. Thus, among so-called "health foods" now on the market there are high-priced special preparations of sun-dried and unsulphured fruits, yet the sulphured dehydrated fruits have now been found, without exception, to be superior in vitamin retention.

# Toxicological.

**Pyrethrum Flowers. IV. Relative Toxicity of Pyrethrins I and II. C. B. Gnadinger and C. S. Corl.** (*J. Amer. Chem. Soc.*, 1930, **52**, 3300–3307.)—Japanese *Pyrethrum* flowers (215 kilos.) were treated according to the method of Staudinger and Ruzicka (ANALYST, 1924, **49**, 288), and 500 grms. of white crystalline mixed semicarbazones of pyrethrins I and II (m.pt. 60° to 90° C.) were obtained. Repeated successive crystallisations from 90 and 60 per cent. alcohol and from a mixture of benzene and petroleum spirit (1:3) yielded 40 and 30 grms. of semicarbazones of pyrethrins I and II, m.pts. 115° to 117° and 54° to 58° C., respectively. The purity of the products were determined by saponification with 100 c.c. of a boiling 1 per cent. solution of sodium hydroxide in 90 per cent. methyl alcohol, acidification, steam-distillation, and titration of the chrysanthemum monocarboxylic acid in the distillate, and of the dicarboxylic acid extracted by ether from the residue in the distillation flask (*vide infra*). The crude pyrethrins were then prepared by digestion of the respective semicarbazones with oxalic acid solution (*loc. cit.*), washed thoroughly with alkali, with potassium permanganate solution and with water, and filtered and distilled *in vacuo* below 40° C. The purity of pyrethrin I ($C_{21}H_{30}O_3$) was determined from the volatile chrysanthemum monocarboxylic acid by the above method, and by the authors' copper reduction method (*id.*, 1929, **54**, 754), and that of pyrethrin II ($C_{22}H_{30}O_5$) from the non-volatile chrysanthemum dicarboxylic acid. Solutions (0·15 to 0·01 per cent.) were made at once in a clear colourless mineral oil (sp. gr. 0·785 at 15·6° C., b.pt. range 180° to 240° C.) and compared with extracts prepared directly from Dalmatian and Japanese *Pyrethrum* flowers stored in the dark. Peet and Grady's biological method was used (ANALYST, 1929, **54**, 49; *J. Econ. Entomol.*, 1928, **21**, 598, 612) 12 c.c. of the oil being sprayed at 25·6° C. at constant pressure (0·88 kgrm. per sq. cm.) through 4 half-inch holes in the ceiling of a cubic chamber (1·83 m. side) with non-adsorbent walls, containing 100 5-day, specially-bred flies (*Musca*

*domestica*). After 10 minutes the flies which have dropped are collected, and the percentage dead recorded after 24 hours at 25·6° C. and 45 per cent. humidity, bread and milk being provided during this period. Pyrethrin II was shown to have a toxicity at least 77 per cent. of that of pyrethrin I, and the copper-reduction method of determination of total pyrethrin content of the flowers is an accurate index of their toxicity. J. G.

# Agricultural.

**Use of Barium Sulphate for Clarifying Soil Suspensions, with Particular Reference to Colorimetric *p*H Determinations. L. D. Baver and C. J. Rehling.** (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 338.)—Pure barium sulphate is useful for clarifying soil suspensions; the amount required to produce flocculation varies with the nature of the soil, sandy soils needing about 0·5 grm. per 25 c.c. of a 1:5 suspension, and clays and loams about 1·0 grm. W. P. S.

# Organic Analysis.

**Determination of the Purity of Acetic Anhydride. C. K. Rosenbaum and J. H. Walton.** (*J. Amer. Chem. Soc.*, 1930, **52**, 3366–3368.)—About 1 grm. of the sample is weighed accurately into a wide-mouthed glass-stoppered bottle, containing about 1 grm. of anhydrous (99·7 per cent.) oxalic acid, 2 c.c. of pyridine dried over barium oxide and calcium hydride added, and the bottle cooled in water to prevent vaporisation of the anhydride. After 10 minutes at 50° C. the excess of oxalic acid is titrated with 0·1 *N* potassium permanganate solution. The equation is $(COOH)_2+(CH_3CO)_2O=CO_2+CO+2CH_3COOH$ (*cf.* Whitford, ANALYST, 1926, **51**, 103), and check experiments by the standard alkalimetric titration method showed that the error is 0·1 per cent. The method is unaffected by small amounts of acetyl chloride, or (if blank determinations are made) by small amounts of oxidising or reducing substances. J. G.

**Fatty Oil of the Bull Frog. S. Tasaki and J. Yamamoto.** (*J. Soc. Chem. Ind., Japan*, 1930, **33**, 233B.)—The constants of bull frog oil were as follows: Sp. gr. at 15° C., 0·9256; acid value, 0·84; iodine value (Wijs), 134·2; $n_D^{20}$, 1·4774; saponification value, 194·8; unsaponifiable matter, 1·25 per cent. The unsaponifiable matter is yellowish, partly solid and contains cholesterol. The mixed fatty acids had iodine value, 114·0; mean mol. wt., 271; ether-insoluble bromides, 8·49 per cent.; and bromine in the ether-insoluble bromide, 58·05 per cent. The fatty acids, treated by the lead soap and ether method, yielded 83 per cent. of liquid, and 17 per cent. of solid acids. R. F. I.

**Use of the Thiocyanogen Value. IV. Analysis of Oils containing Linolenic Acid. 1. Composition of Chrysalis Oil. W. Kimura.** (*J. Soc. Chem. Ind., Japan*, 1930, **33**, 262–264B.)—The unsaponifiable matter (0·98 per cent.) and liquid fatty acids were separated, and the oleic acid determined by the lead salt and alcohol method (Moore, *J. Soc. Chem. Ind.*, 1919, **38**, 320T). Five fractions

were separated, and the iodine values (Wijs) used to obtain the linolic and linolenic acid contents, and thence the thiocyanogen value from the assumption (Kaufmann and Keller, ANALYST, 1929, **54**, 304) that these correspond with 1 and 2 molecules of thiocyanogen, respectively. For the first 3 fractions the experimental thiocyanogen values exceeded the calculated values, owing to contamination with oleic acid, but the last two pairs of results were in good agreement. The percentage composition of the fatty acids was oleic 29·2, linolic 35·9, and linolenic acid 34·9 by the thiocyanogen method, and 29·8, 48·9 and 21·3, respectively, by the author's bromide method (*id.*, 1928, **53**, 352). J. G.

**Acetyl Value of Unsaturated Fatty Oils. S. Ueno and N. Kuzei.** (*J. Soc. Chem. Ind., Japan*, 1930, **33**, 234B.)—The acetyl values of old oils, and also of oils refined with soda and Japanese acid earth (ANALYST, 1929, **54**, 562), have been determined by Lewkowitsch's method (using both the filtration and the distillation processes), also by André's method. The refined oils generally gave lower results than the old oils. The filtration process gave a higher result than the distillation process in all the eleven oils and fats tested, except beef tallow. The higher the iodine value of the oil, the higher the difference between the results of the two processes. This difference in value is attributed to the formation, during acetylation, of easily soluble dibasic acids in the case of the more highly unsaturated oils. When fish oils are being hydrogenated the acetyl value is important, and, in recording it, the method used for its determination should be mentioned. R. F. I.

**Two New Qualitative Tests for Vegetable Tanning Materials. L. Pollak.** (*J. Inter. Soc. Leather Trades Chem.*, 1930, **14**, 299.)—Readings are taken of the wave-length of the light from a 50 c.p. Phillips lamp transmitted through solutions of the tanning extract in layers of increasing height, after treatment of the solution with ammonium sulphide followed by settling and filtration. These readings are plotted against the height of the layer up to the point of total extinction. The curves obtained are characteristic, and enable one to distinguish easily between chestnut and myrobolans; quebracho and mimosa; and, within lower limits, between chestnut wood and oak wood. If magnesium sulphate is present in the extract, it must be removed by the addition of ammonia and ammonium phosphate.

It is found, in applying Stiasny's formaldehyde and hydrochloric acid test, that the presence of large quantities of sulphite cellulose prevents the formation of the precipitate which is characteristic of catechol tans. If, however, an addition is made of 1 grm. of urea prior to the formaldehyde and hydrochloric acid, a positive result is obtained, even if the solution contains only 10 per cent. of a catechol tan (quebracho) with 90 per cent. of sulphite cellulose. R. F. I.

**Analysis of the Dyeing Tannins by the Cinchonine Method. Y. Uyeda.** (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 228B.)—Solutions of Kahlbaum's tannic acid of concentration 0·2 to 0·8 per cent. were treated with 12·5 to 150 c.c. of saturated

cinchonine sulphate, and the percentage of tannin in the resulting precipitate determined by calculation from its nitrogen content. The percentage of tannin in the precipitate was increased in proportion to the cinchonine sulphate used. This variation was also found in the analysis of yashafushi (*Alnus sibirica*). The proportions recommended are 50 c.c. of a 0·4 per cent. solution of the tan and 50 c.c. of saturated cinchonine sulphate solution, under which conditions the precipitate contains 97·00 per cent. of tannin. By this method yashafushi was found to contain 13·6 per cent. of tannin, a result lower than that found by the permanganate method. R. F. I.

**Determination of Chromium, Iron and Aluminium in Chrome Calf Leathers. H. B. Merrill and R. G. Henrich.** (*J. Amer. Leather Chem. Assoc.*, 1930, **25**, 270).—In analysing the mineral matter in chrome leather by the American Official Method, the iron and aluminium are in the trivalent, and the chromium in the hexavalent form. In order to separate the former from the latter, it is necessary to dissolve the hydroxides of iron and aluminium in acid and precipitate a second time with ammonia. If the hydroxides are only precipitated once, chromate is absorbed by them.

The separation of the aluminium from the iron is best effected by dissolving their precipitated hydroxides in 5 *N* hydrochloric acid, neutralising most of the acid with sodium carbonate, adding 1 grm. of sodium peroxide, and boiling until the peroxide is decomposed. The solution is cooled somewhat and filtered, and the precipitate washed ten times with hot water. This treatment effects the complete separation of the two metals. The aluminium in the filtrate is determined by acidifying the solution and precipitating with ammonia in the usual manner. The iron in the peroxide precipitate is difficult to render free from alkali by washing alone. The filter paper containing it is macerated in 10 c.c. of hydrochloric acid and diluted to 100–150 c.c., and the solution is rendered just alkaline to methyl red with ammonia boiled until it becomes pink and filtered. The precipitate is washed thoroughly, dried, ignited, and weighed as $Fe_2O_3$ in the usual manner. R. F. I.

# Inorganic Analysis.

**Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. J. Picard, E. G. Peterson, C. D. Bitting.** (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 294–295.)—For the determination of small quantities of nitrogen oxides, such as are present in the air after the explosion of dynamite in mines, a sample of the air is drawn into an evacuated sampling tube containing 1 c.c. of *N* sulphuric acid, 2 drops of 3 per cent. hydrogen peroxide, and 10 c.c. of water. Nitric oxide is converted into nitrogen peroxide by the action of the air; the peroxide reacts with water vapour to form nitric and nitrous acids, and the nitrous acid is oxidised to nitric acid by the hydrogen peroxide. After two hours, the contents of the sampling tube are washed into a beaker, rendered alkaline with potassium hydroxide and evaporated to dryness. The total nitrate in the dry residue is then determined colorimetrically by means of phenoldisulphonic acid. W. P. S.

**Separation of Lead and Antimony. H. Biltz.** (*Z. anal. Chem.*, 1930, **81**, 81.)—The gravimetric method described in the ANALYST (1925, **50**, 473) should be modified as follows:—The alloy (1 grm.) is oxidised with nitric acid, and the mass taken to dryness. The residue is mixed with 10 grms. of crystallised sodium sulphide and 0·2 to 0·3 grm. of sulphur, and the mass fused as described in the earlier paper. The fusion product is dissolved in a hot solution of ammonium nitrate or potassium chloride; the evaporation with ammonium sulphide has been found unnecessary. The addition of sulphur in the above procedure is important, as it leads to the formation of thioantimonate and, hence, to a better separation.

W. R. S.

**Potassium Titanium Oxalate for the Preparation of Standard Titanium Solution in Colorimetry. W. M. Thornton, jr., and R. Roseman.** (*Amer. J. Sci.*, 1930, **20**, 14–16.)—In preparing a standard solution for the colorimetric determination of titanium based on the yellow or orange colour formed when an acid titanium solution is treated with hydrogen peroxide, the potassium fluotitanate usually employed may be replaced with advantage by potassium titanium oxalate, $K_2TiO(C_2O_4)_2$, $2H_2O$. Sufficient of the recrystallised, air-dried salt to contain 1 grm. of titanium dioxide is mixed with 8 grms. of ammonium sulphate in a 500 c.c. Kjeldahl flask and gradually heated with 100 c.c. of concentrated sulphuric acid, the liquid being finally kept boiling for several minutes. The resulting solution is diluted with water to 800 c.c., cooled, made up to 1 litre, and filtered. Complete destruction of the oxalate is shown by addition of a drop of potassium permanganate solution, which should not be decolorised. The exact titanium content of the solution may be determined by the "cupferron" method. The solution is cheaper and more rapidly prepared than that obtained from the fluotitanate, and does not require the use of platinum vessels. T. H. P.

**Iodimetric Determination of Small Amounts of Zinc. H. A. Pagel and O. C. Ames.** (*J. Amer. Chem. Soc.*, 1930, **52**, 3093–3098.)—For quantities of 3 to 33 mgrms. of zinc per 100 c.c. 1 grm. of solid potassium thiocyanate is added to the solution, followed by 1 c.c. of pyridine, a drop at a time. The solution is stirred at intervals for 1 hour at 20° C., and the zinc is precipitated as $ZnPy_2(SCN)_2$ (Spacu and Dick, ANALYST, 1928, **53**, 508), and the precipitate transferred to a Gooch crucible containing a paper filter-disc with the aid of a solution containing 10 grms. of potassium thiocyanate and 10 c.c. of pyridine per litre, and washed with 10 c.c. of anhydrous ether containing 1 per cent. of pyridine (by volume) below 20° C. The precipitate is then washed into a flask with 150 c.c. of boiling water (the slight amount of zinc hydroxide which may form is ignored), 6 grms. of borax added, boiling continued for 10 minutes, and the stoppered flask cooled under water. The solution is rapidly washed into a second flask containing 50 c.c. of 0·1 *N* potassium iodate solution (*vide infra*), 2 grms. of potassium iodide and 10 c.c. of *N* hydrochloric acid, and, after 15 minutes, the free iodine is titrated

with 0·1 *N* sodium thiosulphate solution in the presence of a further 10 c.c. of 6 *N* acid, with a starch indicator. The reaction is

$$NCS' + 4I_2 + 8OH' \longrightarrow SO_4'' + 7I' + 4H_2O + ICN$$

in alkaline (borax) solution, and upon acidification the cyanogen iodide again reacts with iodide to form iodine and cyanide, giving the final quantitative relation

$$NCS' + 3I_2 + 4H_2O \longrightarrow SO_4'' + 8H^{\cdot} + 6I' + CN'$$

A minimum excess of 5 c.c. of 0·1 *N* iodine solution over that required for the first reaction is essential for the complete oxidation of the thiocyanate under the above conditions. This is ensured by comparing the colour of the iodine in the oxidation mixture containing the sample with that liberated under the same conditions from 5 c.c. of iodate solution, more of the latter then being added to the oxidation mixture, if necessary. The error for pure zinc sulphate solution is −1·4 to +0·3 per cent. Chlorides, ammonium, copper, cadmium, cobalt, nickel, and manganese interfere, but sulphates, nitrates, magnesium and the alkaline earths do not. J. G.

**General Method for the Separation and Determination of Manganese. J. Majdel.** (*Z. anal. Chem.*, 1930, **81**, 14–26.)—The method of v. Knorre—precipitation as manganese peroxide by persulphate—was re-investigated, and in a slightly modified form is recommended as a general procedure for the separation and determination of manganese. By a suitable adjustment of the concentration in sulphuric acid, the co-precipitation of manganites of iron, zinc, calcium, etc., is prevented, but if the quantity of iron present is large, the precipitation should be repeated. Chromium and vanadium are oxidised; hence an additional amount of persulphate is required. Bismuth, tin, and antimony should previously be removed by hydrogen sulphide. Titanium, if present, interferes seriously, owing to hydrolysis; it must be eliminated by suitable methods. Chlorides and nitrates, which interfere, are converted into sulphates by the usual method. The following procedure was worked out:—The acid sulphate solution (maximum 0·15 grm. Mn.) is neutralised with ammonia to the appearance of a slight permanent turbidity, and acidified with 25 c.c. of 3 *N* sulphuric acid. The clear liquid is transferred to a tall 500 c.c. beaker provided with a 250 c.c. mark, treated with 20 to 25 c.c. of ammonium persulphate solution (200 grms. per litre), and diluted to the mark. The covered beaker is heated, and the liquid kept boiling for 15 minutes, with stirring if inclined to bump. The dark precipitate is collected and well washed with hot water, dried in a porcelain crucible, ignited at 940° to 1100° C. cooled quickly by being placed on a cold asbestos mat, as the precipitate increases in weight if kept at about 530° C., by being partly oxidised to $Mn_2O_3$; the precipitate should be brown without black specks. The filtrate is again boiled with 5 c.c. of persulphate solution, as a test for complete precipitation. W. R. S.

**Separation and Identification of the Alkali and Alkaline Earth Metals by means of *Iso*-Amyl Alcohol. H. Yagoda.** (*J. Amer. Chem. Soc.*, 1930, **52**, 3068–3076.)—Metals of the first three groups are removed in the usual way, the

hydrogen sulphide boiled out, and sulphates removed by precipitation with lead nitrate, the excess of which is removed in turn as lead sulphide. Nitrates or chlorides should be the only acid radicals present. The liquid is concentrated to 5 c.c., filtered, the filtrate evaporated with 1 c.c. of 16 *N* nitric acid, and the ammonium salts volatilised. The residue is evaporated at a low temperature with 1 c.c. of 8 *N* hydrobromic acid, pulverised, 3 c.c. of *iso*-amyl alcohol added, boiled for 30 seconds, and the solution filtered at room-temperature. *The residue* (sodium, potassium and barium bromides) is dried, extracted with 1 to 2 c.c. of hot 95 per cent. ethyl alcohol and 2 drops of hydrobromic acid, cooled and filtered. The residue (chiefly potassium bromide) is dissolved in 1 c.c. of water, and the solution tested with sodium cobaltinitrite. The alcoholic filtrate is precipitated with 1 c.c. of 12 *N* hydrochloric acid, cooled, and the precipitate filtered off, dissolved in 2 c.c. of water, and tested for barium with dilute sulphuric acid. The filtrate from the hydrochloric acid should be tested for potassium when less than 1 mgrm. is sought, and the final filtrate (from the barium sulphate) will contain any sodium. *The filtrate* from the amyl alcohol separation contains magnesium, strontium and calcium bromides; it is evaporated to dryness and heated till red fumes of nitrogen peroxide are no longer evolved, and the powdered residue is then leached with 3 c.c. of hot water. The insoluble residue is magnesium oxide and hydroxide, which may be dissolved in acid and precipitated with ammonium phosphate (Otto, *id.*, 1926, **48**, 3016). The residual liquid is evaporated, cooled, 1 c.c. of 16 *N* nitric acid added, the precipitate filtered off on a paper wetted with nitric acid, washed with 0·5 c.c. of acid, and tested for strontium. Calcium in the filtrate is identified by the oxalate test. The solubilities of sodium, potassium and barium bromides in *iso*-amyl alcohol (sp. gr. 0·805) at 25° C. are 0·00085, 0·000014 and 0·00013 grm./c.c., respectively. J. G.

**Determination of Lanthanum. H. J. Backer and K. H. Klaassens.** (*Z. anal. Chem.*, 1930, **81**, 104–106.)—In the analysis of an organic lanthanum salt, high but concordant values were found after ignition of the oxalate to constant weight in a porous porcelain crucible. The ignited substance was found to be the basic carbonate $La_2CO_5$, which is converted to the oxide above 600° C. The carbonate is stable in the interval 400° to 500° C., and can be used in gravimetric work. The oxalate precipitate is collected in a porous porcelain crucible, washed, gently heated until it has lost a transient grey colour and has become white once more, and weighed. Ignition and weighing are repeated ($La_2O_3$ factor, 0·8810). For the conversion of lanthanum oxalate into the oxide, strong ignition for half-an-hour in a platinum crucible over a blast burner is recommended. W. R. S.

**Gravimetric Determination of Potassium as Di-potassium Sodium Cobaltinitrite. A. Wassilieff and N. Matwejef.** (*Z. anal. Chem.*, 1930, **81**, 106–114.)—The following procedure was found to give results varying not more than one per cent. from the quantity of potassium present. The salt is dissolved in 5 to 10 c.c. of water and treated with a few c.c. each of a 25 per cent. solution of cobalt sulphate and a 50 per cent. solution of sodium nitrite; the liquid is stirred

during dropwise addition of 80 per cent. acetic acid, and heated on the water-bath to incipient evaporation; porcelain, not metal, rings should support the basin, otherwise the separated salt decrepitates. After standing overnight, the precipitate is filtered off on a porous crucible, washed with water, dried at 100° C., and weighed as $K_2NaCo(NO_2)_6.H_2O$. If sodium chloride is added before precipitation, the precipitate may be filtered off the same day, after complete cooling. Calcium and magnesium salts do not interfere with the precipitation. W. R. S.

**Modification of the Glycerol Method for Determination of Free Lime. G. E. Bessey.** (*J. Soc. Chem. Ind.*, 1930, **49**, 360–362T.)—The following method is rather simpler than those described previously :—Use is made of a 0·1 *N* solution of benzoic acid in anhydrous ethyl or methylated alcohol, which is stored in a vessel closed to the air and attached to an automatic burette protected by a guard-tube containing phosphorus pentoxide. The burette should have a glass bead valve or pinch-cock in place of a glass tap, as the latter cannot be lubricated satisfactorily with an alcoholic solution. The glycerol used should be of not less than 99·2 per cent. purity, since the ordinary A.R. product, containing about 2 per cent. of water, effects appreciable hydrolysis of compounds of lime in the sample. The glycerol is stored in a vessel attached to an automatic pipette and having a phosphorus pentoxide guard tube. The benzoic acid solution is standardised by pure calcium oxide prepared by igniting precipitated A.R. calcium carbonate at 1000° C. to constant weight; 0·02 to 0·05 grm. of the freshly ignited lime is added to 20 c.c. of the glycerol in a 100 c.c. conical flask, and the latter tightly stoppered by a glass or rubber stopper and well shaken. The lime must be added to the glycerol, as otherwise it may cake and dissolve with difficulty. The flask is kept for 24 hours, with occasional shaking, on a hot plate or in an oven at 60–80° C., all the lime being then dissolved. After addition of 20–30 c.c. of the alcohol, the mixture is shaken and titrated with the benzoic acid solution, with phenolphthalein as internal or external indicator. The end-point is not sharp, but may be read to within 0·2 c.c. of the 0·1 *N* acid.

For actual determinations, sufficient sample to give not more than 0·05 grm. of free lime is added to 20 c.c. of glycerol and treated as above, the indicator being used externally. Normally the sample should remain in contact with the glycerol for 24 hours at 60–80° C., but where the lime content is very low 5–6 hours is sufficient. This procedure yields fairly satisfactory results with sand-lime bricks and unhydrated cements, but has certain possible sources of error. It is not applicable to hydrated materials other than sand-lime bricks, since calcium hydroxide is dissolved only slowly by the glycerol, and, just as with hydrated cements, the small amounts of water formed during the reaction cause uncertain errors in the result. T. H. P.

**Determination of Lithium. M. H. Brown and J. H. Reedy.** (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 304–306.)—Extraction with dry acetone separates lithium chloride completely from its mixture with sodium and potassium chlorides. The extraction should be repeated twice, and between the extractions the mixed

chlorides should be dissolved in a small quantity of water, and the solution evaporated; this treatment liberates any lithium chloride which may be enclosed in the crystals. The united acetone extracts are evaporated, and the residue of lithium chloride is converted into sulphate and weighed. The acetone used for the extraction should be acidified with a drop of hydrochloric acid to prevent the formation of lithium hydroxide, which is insoluble in acetone. W. P. S.

**Determination of Halogen Compounds. J. J. Thompson and U. O. Oakdale.** (*J. Amer. Chem. Soc.*, 1930, **52**, 3466–3467.)—Robertson's method (*id.*, 1930, **52**, 3023) gives low results, and is in general inferior to that of the authors (*id.*, 1195), which has the advantage of being applicable to the analysis of compounds of chlorine, bromine or iodine including metallic compounds and those of low b.pt. An apparatus similar to that described by Willard and Thompson (*id.*, 1893) results in a great economy of time and material; 0·01 to 0·2 grm. of the sample is used. J. G.

**Conversion of Alkali Chloride into Oxalate. N. A. Tananaeff and N. A. Lasarkevitch.** (*Z. anal. Chem.*, 1930, **81**, 117–121.)—On account of certain criticisms, the procedure for converting alkali chloride into oxalate was submitted to re-investigation. The chloride solution is evaporated to dryness with 2 grms. of oxalic acid in a 100 c.c. platinum basin on the water-bath; the basin is covered with a watch-glass resting on bent glass rods. When a crust has formed the mixture is thoroughly stirred with a platinum rod. When completely dry the basin is left uncovered on the water bath for 5 minutes. The sides of the dish are rinsed down, and the evaporation repeated. A third evaporation is always carried out in the same way as the second. The residue contains only traces of chloride; the oxalic acid is volatilised by gentle heating, and the residual alkali oxalate converted into carbonate, as directed by Sörensen. W. R. S.

**Detection of Traces of Fluorine in Rocks. I. P. Alimarin.** (*Z. anal. Chem.*, 1930, **81**, 8–14.)—The process is based on the bleaching effect of fluoride solutions upon zirconium hydroxyanthraquinone complexes (lakes). The reagent is freshly prepared by mixing 3 volumes of zirconium nitrate solution (1 grm. of the salt in 250 c.c. of water) and 2 of alizarine red solution (1 grm. in 100 c.c. of alcohol; the solution is filtered from insoluble matter and the filtrate diluted with 150 c.c. of alcohol); the mixture, which should have a violet-red colour, is diluted with 50 volumes of distilled water. To 2 or 3 c.c. of water in a test tube are added 2 drops of 10 per cent. hydrochloric acid and enough reagent, drop by drop, to produce a plainly visible violet coloration. Another test tube, containing 2 to 3 c.c. of the solution to be tested, is treated as the first. After a few minutes, or an hour if traces of fluorine are in question, the colorations in the two tubes are compared. Fluoride causes a colour change from violet towards lemon yellow, according to its quantity. The sensitiveness is stated to be 0·002 mgrm. of fluorine per c.c. For the detection of fluorine in rocks, 0·2 to 0·5 grm. of the fine powder is well mixed in an agate mortar with 1 grm. of boric anhydride; the mixture is introduced with the

help of a funnel into a hard-glass tube, closed at one end and containing an inner lining of platinum foil; the open end is connected by a short length of rubber tubing with a bulbed U-tube containing water. The extremity near the U-tube is cooled with a wet linen strip. The closed end is introduced into a Penfield furnace (built of loose refractory bricks) and gradually heated with a blowpipe flame until the glass softens (10 to 15 minutes). The end containing the powder is then drawn off. The condensed water and the contents of the U-tube contain all the fluorine as fluoboric acid; the liquid is transferred to a test tube, acidified with hydrochloric acid, and tested as described. W. R. S.

**Determination of Perchlorate. H. H. Willard and J. J. Thompson.** (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 272–273.)—One grm. of the perchlorate, 0·8 grm. of starch and a few glass beads are placed in a flask attached to an upright condenser; an absorption apparatus, containing 1 grm. of arsenious oxide and 100 c.c. of 10 per cent. sodium hydroxide solution, is connected with the top of the condenser. Thirty-five c.c. of concentrated sulphuric acid are added to the flask through a tapped funnel at the top of the condenser, the mixture is heated and boiled for five minutes; 25 c.c. of fuming sulphuric acid (containing 20 per cent. of $SO_3$) are added, the boiling is continued for ten minutes, and saturated permanganate solution is then added slowly to expel any chlorine remaining as hydrochloric acid in the flask. The water is drained from the condenser and the mixture boiled for a further three minutes. The contents of the absorption apparatus are then transferred to a beaker, acidified with nitric acid, treated with excess of silver nitrate solution, and the resulting silver chloride is collected and weighed. The apparatus used is constructed entirely of glass and all the joints are ground in. W. P. S.

# Microchemical.

**Micro-Colorimetric Determination of Glycerol in Coloured Wines. C. de Coquet.** (*Congres Intern. Vigne Vin.*, 1929, 86–88; *Ann. Chim. anal.*, 1930, **12**, 232.)—To 1 c.c. of wine are added 1 c.c. of sodium hydroxide (sp. gr. 1·029), 2 grms. of talc and 10 c.c. of absolute alcohol, the mixture shaken and filtered, and 6 c.c. of the filtrate kept at boiling point for 1 hour, after which 1·5 c.c. of dilute (1:10) sulphuric acid and 2 c.c. of saturated bromine water are added. The mixture is poured into a test tube marked at 10 c.c. and 20 c.c., the volume made up to 10 c.c., the tube warmed for 20 minutes, and the liquid boiled until the bromine fumes have disappeared, when it is cooled and the volume made up to 20 c.c. One c.c. of the liquid and 1 c.c. of a dilute (1:10) alcoholic solution of codeine are placed in a test tube kept in water, and 5 c.c. of sulphuric acid (sp. gr. 1·084) added, the mixture cooled for 10 minutes, shaken, and placed for 5 minutes in a boiling water-bath, after which it is plunged in cold water. After 10 minutes the blue colour is compared with preparations containing standard quantities of glycerol. Red wines are first decolorised with animal charcoal. D. G. H.

**Micro Method for Determination of Cholesterol by Oxidation of the Digitonide. R. Okey.** (*J. Biol. Chem.*, 1930, **88**, 367–379.)—The gravimetric procedure of Windaus (*Z. physiol. Chem.*, 1910, **65**, 110) has for 20 years been considered the standard method for macro determination of cholesterol, but this method has not been applicable to the rapid analysis of the small quantities of blood and tissue usually available for study. The micro combustion developed by Bloor (*J. Biol. Chem.*, 1928, **77**, 63) for the determination of other lipids has offered a method whereby the weighing of the digitonide can be avoided. A micro procedure is described for the determination of free and total cholesterol by oxidation of the digitonide with silver chromate and sulphuric acid, and subsequent titration of the excess dichromate with thiosulphate. Cholesterol has been shown to be altered by the ordinary saponification procedures in such a way that it is no longer quantitatively precipitated by digitonin. A study of the conditions under which a synthetically prepared ester of cholesterol (cholesteryl palmitate) may be saponified with minimal alteration in the cholesterol has been made, and a special procedure for saponification of blood and tissue extracts which conforms to these conditions has been evolved. Attention is called to the fact that, because of this decomposition of cholesterol during saponification, many determinations of cholesterol by precipitation as digitonide from unsaponifiable matter have given results which did not represent the cholesterol originally present in the material.

P. H. P.

**Microchemical Tests in Metallography. M. Niessner.** (*Mikrochemie*, 1930, **8**, 121–130.)—Traces of sulphide sulphur are detected microchemically by Feigl's iodine-azide reaction. *Solutions required.*—(1) The iodine-azide solution is made by dissolving 1·3 grm. of sodium azide ($NaN_3$) in 100 c.c. of $N/10$ iodine solution (12·69 grms. iodine, and 20 to 24 grms. of potassium iodide dissolved in 1 litre of water). This solution is then $N/10$ with respect to iodine and $N/5$ with respect to the sodium azide. (2) The hydrochloric acid mercury silver chloride solution consists of 10 grms. of mercury silver chloride, 20 c.c. of hydrochloric acid of specific gravity 1·124, and 100 c.c. of water. (3) Gelatin paper; a sample should be tested with the iodine azide reagent, as it must not give the sulphur reaction. *Procedure.*—The gelatin paper is dipped for 2 minutes into the hydrochloric acid mercury silver chloride reagent. It is then placed on the mineral section to be tested, which must be clean and fat-free, and is lightly pressed down. After 4 to 5 minutes the paper is removed and thoroughly washed in running water for 30 to 45 minutes to remove the excess of reagent. The test paper is then dried, first with filter paper and then in air at room temperature. On the portion to be tested a drop of the iodine azide solution is added from a small pipette. Where sulphide was present there is an immediate formation of small bubbles of nitrogen, easily visible to the naked eye. After 5 minutes, when the bubbles have ceased to grow, the test may be treated with a drop of ammonia. On the portion of the test corresponding to a part of the original mineral section containing no sulphide, dark nitrogen iodide is formed, but where the iodine azide reaction has taken

place the colour is lighter. When the sulphur content is very high the whole area of the test is colourless. Phosphides give no iodine-azide reaction, and do not interfere with the test. J. W. B.

**Colorimetric Determination of Copper. A. Schachkeldjan.** (*J. angew. Chem.*, 1929, **2**, 475–482.)—The method utilises the intense red colour formed on adding an ammoniacal solution of copper containing sodium salicylate to a solution of potassium cyanide and benzidine in acetic acid solution. A solution containing 0·02 mgrm. of copper in 100 c.c. still gives a red coloration in a 14 c.c. Duboscq cylinder. *Solutions required.*—(1) An acetic acid benzidine solution containing 0·1 grm. of pure benzidine in 100 c.c. of 20 per cent. acetic acid; (2) 1 per cent. potassium cyanide solution; (3) a 3 per cent. solution of sodium salicylate; (4) a 25 per cent. solution of ammonia; (5) a standard copper sulphate solution containing 1·44 grm. of copper sulphate dissolved in 300 c.c. of water containing 1 c.c. of 5 per cent. sulphuric acid; 100 c.c. of this are diluted 10 times. For the test, this solution is further diluted 40 times, so that 1 c.c. contains 0·003 mgrm. of copper. *Procedure.*—Fifty c.c. of the standard solution are mixed with 10 c.c. of the sodium salicylate solution, 10 c.c. of the ammonia solution, 2 c.c. of the benzidine solution, 1·0–1·5 c.c. of the potassium cyanide solution, and finally water to 100 c.c. The colour developed is compared with the test solution similarly treated. As the colour fades, the reading must be completed within 5 minutes. The alkali and alkaline earth metals do not affect the reaction. The heavy metals are removed with ammonia. Silver must not be present. The distilled water must be tested for copper. J. W. B.

**Microchemical Test for Carbonates. F. Feigl and P. Krumholz.** (*Mikrochemie*, 1930, **8**, 131–135.)—The test is carried out in a small glass beaker, 1 cm. in diameter and 3 cm. high; this has a long-handled glass stopper with a small glass knob underneath. The formation of the acid carbonate with carbon dioxide is used to show the presence of carbon dioxide. Pure sodium bicarbonate has $p$H=8·35, and therefore phenolphthalein, which changes colour at $p$H 8–9, is used as an indicator. The reagent used is a mixture of 1 c.c. of $N/10$ sodium carbonate with 2 c.c. of 0·5 per cent. phenolphthalein and 10 c.c. of water. For the test one or two drops of an unknown solution, or a small amount of solid, are placed in the small beaker and 3 drops of 2 $N$ sulphuric acid are added. One drop of the reagent solution is placed on the knob of the stopper, which is immediately fitted over the beaker. In the presence of carbonate the colour of the indicator disappears, the time depending on the amount of carbonate present. When only very small amounts of carbonate are present a control test must be carried out, owing to the presence of carbon dioxide in the air. Two drops of a carbonate solution containing 4$\gamma$ of carbon dioxide (dilution 1:25000) decolorised the indicator in 10 minutes. Volatile acids, such as hydrogen sulphide, sulphur dioxide, hydrocyanic acid, nitrous acid and acetic acid, disturb the test by decolorising the indicator. The presence of hydrogen sulphide and sulphur dioxide can be tested in the same apparatus, before the carbonate test is carried out. A

drop of a solution of 0·5 grm. of ferric ammonium sulphate and 0·1 grm. of potassium ferricyanide in 100 c.c. of water is placed on the knob of the stopper, and the test substance treated with 2 drops of sulphuric acid. When sulphur dioxide or hydrogen sulphide is present, the reagent solution is turned blue, owing to the formation of Berlin blue; for 1$\gamma$ of hydrogen sulphide and 2·5$\gamma$ of sulphur dioxide the colour change is distinct in 10 minutes. To detect carbonates in sulphites and sulphides, these must first be oxidised to sulphates. A drop of the saturated sulphite solution, or 5 per cent. sulphide solution, is shaken with 2 drops of 10 per cent. hydrogen peroxide, and then acidified with 2 drops of 2 *N* sulphuric acid. Carbonates may be tested in the presence of cyanides by converting the cyanide into mercuric cyanide, which does not give free hydrocyanic acid with dilute acid. Four drops of saturated mercuric chloride are added to one drop of cyanide solution (not stronger than 5 per cent.) and, after shaking, 2 drops of 2 *N* sulphuric acid are added. These tests for carbonates are useful for testing the carbonate content of technical chemicals. The test can also be used for oxalic acid, by treating the test solution with a drop of 2 *N* sulphuric acid and a saturated potassium permanganate solution. The oxalic acid is oxidised to carbon dioxide, which decolorises the indicator in the usual way; 5$\gamma$ of oxalic acid (concentration 1:10,000) decolorise the indicator in 10 minutes. When carbonate and oxalic acid are both present, the carbonate is first destroyed by heating with sulphuric acid, before adding the permanganate. J. W. B.

# Physical Methods, Apparatus, etc.

**Phosphoric Acid for the Determination of Melting Points. F. D. Snell.** (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 287.)—A bath containing syrupy phosphoric acid, in place of sulphuric acid, is recommended. Phosphoric acid begins to lose water at 100° C., and the bubbles of steam cause circulation in the bath. The evolution of steam continues up to nearly 300° C. On cooling, if 200° C. has not been exceeded, about 10 per cent. of water are stirred in below 100° C., and the bath is again ready for use. If heated to 250°–300° C. the liquid tends to gelatinise when cooled, but, if treated with water and warmed, it will become homogeneous. W. P. S.

**Optical Analysis of some Colloidal Solutions of Silver and Discussion of the Results obtained. F. Rimattei.** (*Rev. Gén. Colloïdes*, 1930, **8**, 145–160.)—The extinction coefficients ($e$) at 20° C. of solutions of argyrol (a colloidal compound prepared from silver nitrate and vitelline, and containing about 20 per cent. of silver) of concentration ($c$) $10^{-3}$ to $10^{-5}$ (grm. per litre?) were measured in an Yvon spectrophotometer for wave-lengths between 495 and 700$m\mu$, with an error of 1 per cent., the best results being obtained for $\lambda$ 550$m\mu$. The values of $e$ and $\lambda$ were then plotted for the various concentrations employed, and the curves obtained shown to be analogous in form and to indicate a large continuous absorption band, with a maximum in the ultra-violet region. The graph showing the

relation between $e$ and $c$ for $\lambda\ 550m\mu$ is a straight line for the concentrations $1{\cdot}0\times10^{-3}$ to $0{\cdot}2\times10^{-3}$, the value of the ratio $e/c$ being 1·830 to 1·898 over this range. The values of $e$ are not appreciably affected either by change in temperature over the range 10° to 28° C., or by the age of the solution (up to 2 days). These curves were then used to determine the strengths of unknown solutions of argyrol from their measured extinction coefficients, a relative error (compared with the gravimetric method) of 1 to 4 per cent. being obtained for solutions of concentration $0{\cdot}6\times10^{-3}$ to $0{\cdot}00857\times10^{-3}$. The brown colour was also matched in a Duboscq colorimeter against that of a measured depth of standard of known strength, but the error in this case was 4 to 8 per cent., whilst for visual comparison of the colour of a solution (concentration $0{\cdot}00857\times10^{-3}$) with the colours of a series of standards it was 13 per cent. The theoretical degrees of precision of the instruments concerned were then calculated by application of the laws of photometry, and the resulting values shown to be in agreement with those obtained by experiment. J. G.

**Colour Measurements of Tanning Extracts. A. de la Bruère.** (*J. Inter. Soc. Leather Trades Chem.*, 1930, **14**, 315.)—In the Toussaint photo-electric colorimeter (*J. Int. Soc. Leather Trades Chem.*, 1928, **12**, 485) it is important that the voltage supplied to the illuminating lamp should be kept constant, that the voltage of the accumulators connected with the photo-electric cell should be constant during comparative readings, and that electrical leaks should be avoided. The colorimeter is now provided with screens, as nearly monochromatic as possible, in red, orange, yellow, green, blue, indigo, and violet. Measurements by this instrument have been made of the colour of four tanning materials at different concentrations, and in eight materials at the same concentration. The figures given in the tables represent the percentage of the light passing through the solution compared with that passing through water. R. F. I.

**X-Ray Examination of Lithopones. W. A. Wood.** (*J. Soc. Chem. Ind.*, 1930, **49**, 300–301T.)—Since the crystalline grains in a fine powder are oriented chaotically, an almost monochromatic pencil of $X$-rays of wave length $\lambda$ will be certain to strike some of them at the angle ($\theta$) necessary to fulfil the conditions of Bragg's relation $2d \sin\theta = \lambda$, where $d$ is the spacing of the reflecting planes. A spectrum of lines is thus produced characteristic of the substances present, and since the positions of these lines are known, $\theta$ may be found and thence $d$. Comparison with spacings calculated from substances of known structures enables a specimen to be identified, while, since the relative breadth of the spectrum lines depends on the number of reflecting planes in each grain, the breadth of the lines is an indication of the average grain size. Sub-microscopical grains (*e.g.* in pigments) give this diffused type of line, and an irregular arrangement of the intensities of the lines indicates deviation from a random arrangement of particles in the sample. The radiation from the copper anticathode of a water-cooled $X$-ray tube was passed through thin nickel foil, the sample being mounted by means of an adhesive so as to form a cylinder 0·5 mm. in diameter on a hair placed

along the axis of a cylindrical camera of 5 cm. radius, on the circumference of which was bent the photographic film. The photographs from zinc lithopone, and from barium sulphate and zinc sulphide, both chemically co-precipitated and mechanically mixed, were substantially identical, and it is inferred that lithopone is a mixture of its constituents and not a compound. This, however, requires some qualification, since its pigment properties differ from those of the mixture. Cadmium lithopone, prepared from cadmium sulphide, gave similar results.

J. G.

**Magnesite: its Application in Assaying. R. J. B. Kethel.** (*J. Chem. Met. and Min. Soc. S. Afr.*, 1930, **30**, 323–329.)—In making cupels, whether using a glue or a sugar solution, too much of this should not be mixed with the magnesite, since otherwise the cupels lose in porosity; if too little is used, the cupels will be soft and will crumble readily. A good plan is to mix the magnesite with a little warm water and, as the cupels come from the machine, to dip them in a 1 per cent. sodium silicate solution, to dry them on a tray in an oven at about 100° C. for 12 hours, and to leave them to dry thoroughly. The silicate closes the pores and prevents absorption of carbon dioxide during drying, and makes the cupel smoother and harder. Some cupels may absorb as much as their own weight of lead oxide, but it is inadvisable to run the risk of scoria formation by using cupels deficient in weight. When 52–53 grms. of lead were taken with cupels weighing 61·5–64 grms., 86·2–87·6 per cent. of the lead was absorbed, and the remainder volatilised. With cupels weighing 61–65·5 grms. from a second manufacturer, from 53 to 57·2 grms. of lead were cupelled, 89·1–91·5 per cent. being absorbed.

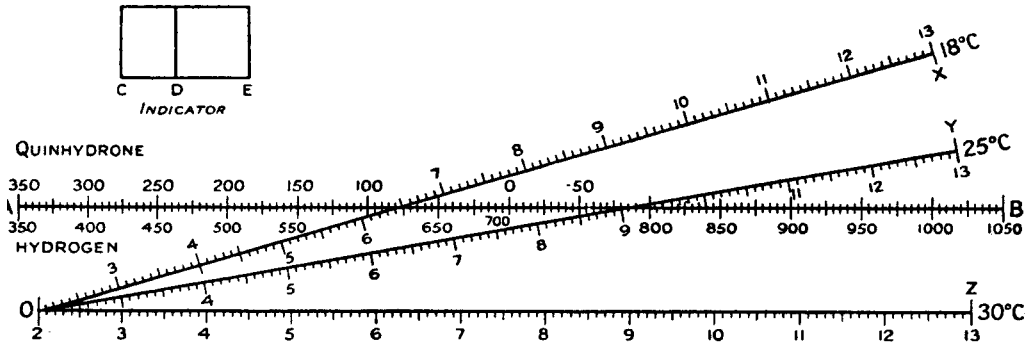
Cement is not to be recommended as a base in making cupels, as it does not combine well with the magnesite powder, and there may be subsequent cracking; moreover, the cupellation is slower and demands a higher temperature, with increased loss of gold.

Magnesia, obtained by calcining magnesite at 800° C., crushing and sieving, may be used as a bed in reverberatory and muffle furnaces. The coarse material is spread in a thick layer over the hearth of the fusion furnace before the crucibles are introduced, the furnace tiles being thus protected. The finer material is placed on the bottom of the muffle to absorb any excess of lead, the life of the muffle being thus prolonged. A 6:1 mixture of cupel powder and caustic magnesia may be used on repair work to furnaces and muffles, boric acid or sodium silicate serving as a binder.

T. H. P.

**Ruler for the Interconversion of Electromotive Force Readings and *p*H Values in the Electrometric Measurement of Hydrogen Ion Concentration. J. Grant.** (*J. Soc. Chem. Ind.*, 1930, **49**, 302T.)—An indicator is made by marking off distances corresponding with the positions of the lines *C*, *D* and *E* (corresponding with the saturated, *M*– and 0·1 *M*-calomel electrode, respectively), along the edge of a card, or by scratching the lines on a sheet of glass. The vertical line corresponding with the particular calomel electrode in use is then placed so that it cuts the scale *AB* at the point denoting the electromotive force (in millivolts) of the

cell, the top scale being used for the quinhydrone electrode, and the lower for combinations of hydrogen electrode and calomel electrode. Then the vertical line $C$ cuts the scales $OX$, $OY$ and $OZ$, which correspond with the temperatures 18°, 25°




and 30° C., respectively, at the required $p$H value. For the conversion of $p$H values into millivolts, the procedure is reversed, *i.e.* $C$ is placed in position at the $p$H value on the appropriate temperature scale, and the reading on $AB$ is then given by the line on the indicator for the electrode used. For greater convenience, the nomogram is used in the form of a ruler with a glass cursor. The error is usually about 0·02 $p$H unit, but for a few combinations rises to 0·06. J. G.

# Reviews.

A Text Book of Dairy Chemistry. By Edgar R. Ling, M.Sc., A.R.C.Sc., F.I.C. Pp. 213+vii. London: Chapman & Hall. Price 6s. net.

Strictly speaking, this is a text book for the use of students in agricultural colleges; it is written in simple style so as to be as intelligible as possible to those who may have but a moderate knowledge of chemistry and allied subjects, and the experimental part describes comparatively straightforward operations, many of which are of the nature of instructive demonstrations.

This text book for students is, however, a work so admirable of its kind that it may well appeal to a larger circle than that for which it was obviously intended. For instance, in the sections on milk composition, statistics and legal standards for milk, there is some very sound and useful criticism of traditional concepts, and sections such as those on the freezing-point method for milk control, the creaming of milk, and the action of rennet embody the results of important researches which have appeared quite recently. At the end of some of the chapters is a list of references to original papers. In short, the value of this book to students and

others lies in the fact that the author is obviously in the habit of taking very little for granted, and also in his ability to present successfully in a few words the results of reading which must have occupied at least as many hours.

P. S. ARUP.

THE MEASUREMENT OF HYDROGEN ION CONCENTRATION. By JULIUS GRANT, Ph.D., M.Sc., A.I.C. Longmans, Green & Co. Pp. 159. Price 9s.

Although the last few years have seen the publication of a number of books dealing with the subject of hydrogen ion concentrations, these have been written from what may be termed the "academic" point of view. It is true that industrial applications have been discussed quite fully in some of them, but the treatment has been such as to interest more particularly those engaged in research and development. For the works chemist or analyst concerned mainly with routine and control work such books would probably seem to be rather formidable. Hitherto, as the author of the book under review says in his preface, "the worker in the industrial laboratory who has little or no knowledge of electrochemistry, but who feels that a study of hydrogen ion concentrations is essential for his purpose, has been in an unfortunate position" in not having a book written specially to satisfy his requirements. Dr. Grant has made a very praiseworthy attempt to rectify this situation, and, in the course of some 150 pages, has given an excellent survey of the theory and practice of the measurement of hydrogen ion concentrations.

The book is divided into four parts, each of which concludes with a number of useful and up-to-date references; the first part consists of a short outline of electrochemical theory, with special reference to the main subject of the book. The second and third parts deal with the theory and practice of electrometric and colorimetric methods, respectively, for the determination of hydrogen ions. In the last section lies the real justification for the publication of the book; whereas the previous chapters have discussed general experimental aspects, this section deals with the methods and technique used by the works' chemist and the analyst engaged in the control of industrial processes. The examples show how hydrogen ion measurements are made in connection with agriculture, analysis, biochemistry, fermentation and allied industries, foodstuffs, leather industry, metallurgy, paper, pharmacy and water. The book can be warmly recommended to the busy practical man, with only a general knowledge of chemistry, who is interested in the subject of hydrogen ion concentrations.

S. GLASSTONE.

DIE MASSANALYSE. ERSTER TEIL: DIE THEORETISCHEN GRUNDLAGEN DER MASSANALYSE. (The Theoretical Foundations of Volumetric Analysis.) By I. M. KOLTHOFF. Zweite Auflage. Berlin: Julius Springer. Pp. 277. Price 13.80 marks.

The appearance of the second edition of this most interesting book so soon after the first (see ANALYST, 1927, **52**, 663) shows that it has proved popular—

and quite deservedly—among chemists. The new edition follows exactly the lines of the old, but twenty-three pages of new material have been added; the subject of oxidation-reduction receives fuller treatment, and short accounts are given of Böeseken's "dislocation" theory of catalysis, of Christiansen's view on chain reactions, and of the recent work of van der Steur on the addition of iodine to unsaturated fats and fatty acids. The references have all been brought up to date. The first edition of this book, with some additions, has been translated into English (see ANALYST, 1929, **54**, 194).

S. GLASSTONE.

DIATOMACEOUS EARTH. By ROBERT CALVERT. Pp. 251. New York: Chemical Catalog Company. Price $5·00.

This work is one of the series of monographs published under the auspices of the American Chemical Society, and the subject is an appropriate one, as the United States of America produce more than seventy per cent. of the world's total output, which in the year 1926 amounted to about one hundred and ten thousand long tons.

The selection of Mr. Calvert as the author of this monograph was a happy one, as his name is closely associated with researches and patents in connection with the properties and applications of diatomite—he was formerly in charge of the research laboratory of the Celite Company, Lompoc, California, one of the principal producers of diatomite, and of materials composed of it.

The book is well written, and so full of interest that the reviewer concluded his work of reading it with some regret. Relatively little violence is done either to English spelling or construction, although we meet with "center," "luster," etc., and some unusual phrases, such as that on p. 23, ". . . followed each other into the discard." The errors are few, but we have to call attention to the reference to Table 14, instead of 13, on page 31, and to an error in the calculation on page 196; otherwise the revision has been well done, and printer's errors are rare.

There is much material in this work which will be useful to the analyst; although methods of analysis do not find a place in it, abundant references are made to the composition of diatomite occurring in various parts of the world, to the influence of impurities in the natural earth upon its properties and uses, and the book contains much information upon both the industrial applications of diatomite and the articles of commerce which contain it; how numerous these are will come as a surprise to many.

As the structure of the fossil diatoms is a very important matter, taken in conjunction with the impurities occurring in the diatomite, in determining the suitability of a diatomaceous earth for any specific purpose, it is to be regretted that the photomicrographs are not better produced; some of the prints are indistinct, and they have been obtained by a variety of magnifications, and in some cases the magnifications are not stated.

The author corrects the impression that infusorial earth is a correct synonym for diatomaceous earth, as it contains no fossils of infusoria, and he points out that dynamite is no longer made in the United States by absorbing nitroglycerin in diatomaceous earth. Analysts will be interested in the uses of diatomite as a filter-aid, in the filtration of oil-water emulsions, and of substances in colloidal solution, also in the behaviour of its silica when diatomite is heated alone, when heated with substances in aqueous solution, or when fused with them. The subjects of filter-aids, filter media, filtration, absorption, insulation against loss and gain of heat are treated very fully, and the information on these matters will be of interest to consulting chemists and engineers.

Students in chemical technology will do well to read this book, which is written in a style well calculated to promote research, which is one of the two main objects the American Chemical Society has in the production of these monographs. Mr. Calvert is to be congratulated in having produced a book which includes so much information in so few pages. The references to chemical and patent literature are numerous, and the name and subject indexes are very complete.

H. CHARLES L. BLOXAM.

ELEMENTARY INORGANIC CHEMISTRY. By J. W. MELLOR, D.Sc., F.R.S. London, New York and Toronto: Longmans, Green & Co., Ltd. 1930. Price 3s. 6d. net.

It was suggested to the author that a book a little more advanced than his *Introduction to Modern Inorganic Chemistry* would better meet general requirements, and that one a little smaller would be more suitable for beginners. The suggestion was a good one, since the latter half of it resulted in the present volume, which starts with the elements of chemistry and takes the reader almost to matriculation standard.

The author's aim, however, has been, not so much to cover ground, as "to get home a few important facts, to develop a habit of reasoning from the facts, to maintain interest and to whet the appetite for more." These aims, particularly the last, have been achieved through the medium of an easy style, seasoned with a judicious mixture of accurate facts, practical illustrations, and appropriate quotations and anecdotes. For example, fundamental subjects, such as the nature of air, are treated historically, *i.e.* the methods and conclusions of successive workers from Aristotle onwards are considered (with portraits and interesting biographical notes), and the line of reasoning by means of which the final correct conclusion was attained is thus clearly traced. Again, in connection with the section on circumstantial and cumulative evidence, the student is recommended to study certain of the works of Poe—a piece of advice which should at once win for the book a measure of popularity.

The illustrations, which are pictorial, and show the apparatus of the alchemists as it should be shown, serve the same end. The vivid representations of

the effects of a hydrogen explosion and of smelling concentrated ammonia should serve as warnings to the budding chemist—unless of course they tempt him to test their accuracy for himself! A novel method of illustration is the superposition on a photomicrographic field of crystals of the outline of an "ideal" crystal.

A few points which may confuse the beginner require attention. On p. 39 the wording may be taken to imply that sodium is cut under water in a manner similar to that described for phosphorus; the polarity signs of Fig. 37 (p. 53) are reversed, and the rendering on p. 60 of the saying of Democritus relating to the indestructibility of matter ("nothing can ever become something, nor can something become nothing") obviously requires amendment. The cross-reference on p. 103 should refer to p. 79 and not p. 8, and that on p. 185 to Fig. 63 and not Fig. 32.

Apart from this and a few obvious misprints, neither the subject matter, standard of production nor price leaves grounds for criticism, and the book may be safely commended to the teacher as desirable in every way for the beginner.

JULIUS GRANT.

ALCOHOLOMETRY. By FRANCIS G. H. TATE. With an Historical Introduction by the Author and GEO. H. GABB. Pp. 90, Index and Illustrations. Pub. by H.M. Stationery Office. Price 5s.

This small volume gives, for the first time, a full account of the history and the theory of the official method of determining alcohol in spirituous liquors.

It tells an intriguing story, running through two centuries, of a problem which, when it first arose, must have seemed almost insoluble. It meant determining, in aqueous solution, a compound about which there was little knowledge with a number of others of which there was less. Absolute alcohol had not yet been prepared, and even the word alcohol had not its present use.

Apart from crude tests based on inflammability or on surface tension phenomena, the only available means depended on the density of the liquid. The general idea of the specific gravity had been known from the earliest times, but no quick method for ascertaining it was available, other than by the use of the hydrometer. This had the merit of being small and portable, reasonably strong and fool-proof, not too costly, and reproducible in large numbers with the needful accuracy.

Its invention has been attributed to Robert Boyle, but there is good evidence of the existence of a glass instrument in Roman times. In any case the brass one, devised by John Clarke, in 1725, was in semi-official use for Revenue purposes for some years, was legalised in 1787, and, until the present day, what is in all essentials the same instrument is still employed.

With the growth of knowledge and experience drawbacks and defects became apparent in the application of the instrument, and this book shows how most of them were overcome.

The very interesting historical introduction of 18 pages briefly sketches the origin of distillation and of distilled spirits, and also of the early methods for the evaluation of such spirits, up to the end of the seventeenth century, with useful references to original sources.

It does not pretend to be exhaustive, but some reference might well have been made to an excellent paper by Fairley (ANALYST, 1905, **30**, 293), an important and admirable volume of 236 pages, entitled "Recherches Rétrospective sur l'Art de la Distillation Historique de l'Alcool, de l'Alambic et de l'Alcoométrie," by Dujardin, 1900, and, by the same author, "Instruments de Precision appliques a l'oenologie," 1928, each with many illustrations and copious bibliographical notes.

The historical section of the volume under review is clearly written, well arranged, and gains much in interest from the illustrations of early instruments and hitherto unpublished manuscripts in Mr. Gabb's unique collection, which, however, only whets one's appetite for further plates of the 50 or 60 hydrometers which appeared during the eighteenth and nineteenth centuries, such as those of Bate and of Boriés and the rival instruments put before the Committee of Enquiry in 1802. It is to be regretted that in the short bibliography on pp. 89 and 90 references to continental work are relatively few, and this may account for the claims of Homberg (1652–1715) to be the first to make commercial use of the specific gravity bottle, having been overlooked in favour of Richardson (1788).

The book as a whole deserves, and indeed demands, a more adequate index, and headings at the top of each page would have added much to the ease of reading.

In some of the paragraphs dealing with the more recondite subjects the phraseology is neither too happy nor too clear. Examples are on p. 66 relating to interpolation on p. 67, on the difficulties arising out of the different rates of expansion of alcohol and water, and on pp. 73–75 on surface tension.

There are few misprints:—"Intrapolation" instead of "Interpolation," though both forms appear on p. 62. On p. 21, "contraction" instead of "concentration," seems desirable, and on p. xii capacity is meant not "volume." These, however, are trifling matters, and the standard of production as a whole is all that could be desired.

The book should be of great interest to the Public Analysts and other chemists, from the historical, as well as from the scientific side. It is only to be regretted that so much careful thought had to be spent on a system based on "proof spirit," which may have been a great achievement when the phlogiston theory flourished, but which only the dead hand of authority could have perpetuated until now.

CECIL H. CRIBB.