

THE ANALYST.

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

OBITUARY NOTICE.

JOHN HUGHES.

JOHN HUGHES, a very old member of the Society, who died on June 4 in his seventy-seventh year, was the son of the Reverend Isaac Hughes, Vicar of Mynyddysiwyn in Monmouthshire, and was educated at the Usk Grammar School and at the well-known Agricultural College of Cirencester, where he developed a special taste for Agricultural Chemistry, and became assistant to the then Professor of Chemistry, the late Dr. Augustus Voelcker.

When Dr. Voelcker retired from his Professorship and migrated to London, to be in closer touch with his duties as consulting chemist to the Royal Agricultural Society of England, John Hughes accompanied him, and remained a member of his staff until 1872, when he became chemist in the works of Lawes' Chemical Manure Company, where he remained until 1877, in which year he was engaged by the Ceylon Planters' Association to go to Ceylon and to make a comprehensive investigation, from the chemical point of view, of the problems affecting the growth and manuring of the coffee plant. The result of his labours was embodied in an exceedingly useful report to the Association, which was published in book form in 1879.

On his return from Ceylon, while continuing to advise Lawes' Chemical Manure Company, Hughes established himself in independent consulting practice in Mark Lane, in which practice he was actively engaged, without interruption, until a few weeks before his death.

During this period of more than forty years his attention continued to be mainly devoted to the chemistry of soils and fertilisers, and he was responsible for the introduction into the manure market of a material to which—perhaps illogically from a chemical point of view—he gave the name of "Basic Superphosphate." This consisted of superphosphate in which the soluble phosphate was converted into a "reverted" or "precipitated" form by grinding into the superphosphate a sufficient quantity of lime, thus producing a very readily available form of non-acid phosphate for use on soils deficient in lime, for which ordinary superphosphate, by reason of its acidity, might be unsuitable, especially for turnips, cabbages, and other cruciferous

crops liable to the disease known as "finger and toe." The development of the supply of basic slag, and its general use as a substitute for superphosphate in such cases, however, prevented the development of the production of basic superphosphate on anything like the scale which it might have assumed under other circumstances; but it is still produced by some of the leading fertiliser manufacturers, and by reason of its more ready availability is considered to possess, apart from the question of cost, advantages over basic slag of corresponding phosphatic content.

Hughes joined the Society of Public Analysts at an early period of its history, and served on its Council from 1891 to 1894, though of recent years his attendance at the Society's meetings had become irregular. He was also amongst the earliest Fellows of the Institute of Chemistry, on the Council of which he served from 1891 to 1894 and from 1897 to 1900.

He held the appointment of Official Agricultural Analyst for the County of Hereford, and took an active interest in all matters relating to the administration of the Fertilisers and Feeding Stuffs Act.

BERNARD DYER.



ESTIMATION OF POTASSIUM IN PRESENCE OF SODIUM, MAGNESIUM, SULPHATES AND PHOSPHATES.

BY H. ATKINSON, B.A., A.I.C.

(Read at the Meeting, May 4, 1921.)

THE method depends upon the relative solubilities of these salts, and the perchlorates of the metals, in methyl alcohol. Potassium perchlorate has a low solubility in this liquid, whilst the perchlorates, sulphates, and phosphates of magnesium and sodium have a sufficiently high solubility to make the separation possible.

The procedure is as follows: The mixture of salts is evaporated in a 300-c.c. beaker with perchloric acid until fumes of the acid are evolved, and to ensure complete removal of hydrochloric acid, if present, the evaporation with perchloric acid is repeated; 100 c.c. of methyl alcohol are added, and the solution is maintained at the boiling-point, with occasional stirring, for one hour. It is then allowed to stand overnight, and filtered through a Gooch crucible, the transference and washing being effected with 50 c.c. of methyl alcohol acidified with perchloric acid in the ratio of 95 alcohol : 5 perchloric acid (sp. gr. 1.12), and finally with about 20 c.c. of ethyl alcohol.

A blank experiment was made with pure potassium perchlorate, and the loss due to the solution of the salt was 0.014 gm., but when other salts are present small quantities are held out of the solution by potassium perchlorate, and the loss is thereby compensated to a certain extent.

It is evident that so long as the quantities of the radicles named are well within the limits of their solubility the determination of potassium as perchlorate is possible.

The limit of solubility of these radicles was determined by taking an excess of a mixture of magnesium sulphate and sodium phosphate (about 3 grms. each) and, following the procedure already stated, evaporating off the alcohol from the filtrate, dissolving the residue in water, diluting the solution to 250 c.c., and determining the amounts of the different radicles in aliquot portions.

The proportions in the total filtrate were: Magnesia (MgO), 0.228 gm.; sulphates (H_2SO_4), 0.54 gm.; and phosphates (P_2O_5), 0.928 gm.

The quantities of salts used in test experiments were: (a) 0.500 gm. potassium chloride, and 1 gm. sodium sulphate, $Na_2SO_4 \cdot 10H_2O$; and (b) 0.499 gm. potassium chloride, 0.6 gm. magnesium sulphate, $MgSO_4 \cdot 7H_2O$; and 1.1 gm. sodium dihydrogen phosphate, NaH_2PO_4 .

The weight of potassium perchlorate obtained in each experiment was 0.924 gm., corresponding to: (a) 99.4 per cent. potassium chloride, and (b) 99.6 per cent. potassium chloride.

PUBLIC HEALTH LABORATORIES, CAIRO.



THE JOINT USE OF TWO INDICATORS IN THE TITRATION OF ACIDS AND BASES.

BY J. L. LIZIUS, B.Sc., A.I.C.

(*Read at the Meeting, June 1, 1921.*)

It has been found that accurate titrations can be readily obtained, by the joint use of two indicators, where colour changes denote either the approach of the end-point or that the titration has been overshoot.

1. *Titrations where Phenolphthalein is used as the Indicator.*—One drop of phenolphthalein (0.5 per cent.) and 3 drops of thymolphthalein (0.04 per cent.) are added to the acid solution to be titrated. The end-point is denoted by a pink colour (P_{11} 8.3). On the addition of a further drop of $\frac{N}{10}$ alkali, the solution becomes a violet colour, produced by the combination of the pink colour of phenolphthalein with the blue colour of thymolphthalein (P_{11} 10). Thus, if the end-point has been overshoot by 1 drop of $\frac{N}{10}$ alkali, this will be denoted by a violet colour, and the correct titration can be obtained by back-titration with $\frac{N}{10}$ acid, 1 drop at a time until the colour of the solution changes from violet to pink.

Similarly, in the titration of alkaline solution, when phenolphthalein is used as the indicator, it is advantageous to add thymolphthalein. The approach of the end-point is denoted by the colour change violet to pink, and the acid is then added 1 drop at a time until the pink colour disappears.

2. *Titrations where Methyl-red is used as the Indicator.*—One drop of methyl red (0.02 per cent.) and 3 drops of thymol-blue (0.04 per cent.) are added to the acid solution to be titrated. The end-point is denoted by an orange colour (P_{11} 6). On the addition of a drop of $\frac{N}{10}$ alkali the solution becomes yellow, and a further drop of alkali produces a blue-green colour (P_{11} 9), due to the thymol-blue.

Thus, if the end-point has been overshoot by 2 drops of $\frac{N}{10}$ alkali, this will be denoted by a blue-green colour, and the correct titration can be obtained by back-titration with $\frac{N}{10}$ acid, 1 drop at a time, until the neutral orange tint is obtained. The methyl-red-thymol-blue combination is, however, more useful where alkaline solutions are to be treated with $\frac{N}{10}$ acid. The solution is blue, and as the end-point is approached, the colour changes from blue to green. Another drop of $\frac{N}{10}$ acid causes a colour change, green to yellow, and one more drop of $\frac{N}{10}$ acid is required to obtain the neutral orange tint.

It was found that the addition of 3 drops of the auxiliary indicators had no effect whatever on the titration values.

ANALYTICAL AND RESEARCH DEPARTMENT,
ALLEN AND HANBURY'S, LTD.



THE SPECTROMETRIC EXAMINATION OF CERTAIN FIXED OILS AS A MEANS OF IDENTIFICATION.

BY HERMANN C. T. GARDNER.

(*Read at the Meeting, June 1, 1921.*)

IN view of the conflicting statements made by Allen (*Comm. Organic Analysis*, Third Edition, II., p. 26), by Lewkowitsch (*Chemical Analysis of Oils, etc.*, Second Edition, p. 113), and by Doumer and Thibaut (*Corps Gras Industrielles*), it is obvious that any spectroscopic examination of any fixed oil exhibiting absorption bands is untrustworthy if reliance be placed upon the presence, or absence, of such phenomena for diagnostic purposes; and, as several fixed oils do not yield any absorption bands at all, simple spectroscopic examination alone would appear practically valueless as a means of identification. From what has been accomplished so far the only use of the spectroscope would seem to be for the purpose of placing an oil in a particular class—a waste of time so far as analytical procedure is concerned.

The observations recorded from my investigations are not proffered as conclusive, as, obviously, repeated examinations of similar oils from dissimilar sources are requisite before a table of definite limits of absorption or the ranges of visibility of the spectra of fixed oils could be accepted as infallible. Such a table, if free from error, would doubtless assist in the speedy identification of a fixed oil because it would prove discriminative.

With the foregoing reservation, my observations tend to show that dissimilar oils exhibit dissimilar limits of visibility under similar conditions, whilst oils of the same kind show practically identical spectra as regards length—that is, in the extent of the visibility of their spectra—under like conditions. Herein lies the true value of Allen's remark, that "no oils of animal origin give definite absorption bands, the spectrum being merely obscured at the more refrangible end."

METHOD.—The instrument used was a Browning's Student's Spectroscope fitted with a $1\frac{1}{4}$ -inch dense prism and provided with an arc of 100° divided into thirds of

a degree, having a vernier and lens, thus permitting angular measurements of the position of the axis of the telescope to be made.

The readings were taken of such angular measurements by bringing the telescope into such a position that one of the cross wires in the eye-piece, when in a vertical position, coincided with the extreme edge of the visible spectrum, so that on one side was the barely visible limit of the spectrum and on the other obscurity; or in the case of an absorption band, when the band was sufficiently wide to be conveniently measured, by bringing the wire into coincidence with the extreme edges of the band alternately. If the bands were not of such a breadth as to permit of this, the wire was brought into apparent superimposition; in each instance the reading on the scale of the arc was noted.

Measured in this manner, the length of the visible spectrum of white light was found to occupy a segment of the arc, beginning at the red end at 43° and ending at the violet at 47.6° . The range of the spectrum was thus 4.6° . The position of the sodium, or D line, was experimentally ascertained to be precisely at 44.3° , corresponding to division 50 on Bunsen's scale.

The apparatus consisted of dull black metal troughs of various lengths (usually 3 or 6 inches), having a window of clear white glass at either end. The window intended for use near the slit of the spectroscope was surrounded by a collar into which the collimator-tube of the instrument could be inserted, and on the end of the trough, remote from the spectroscope, a box-like attachment was constructed to receive the source of light.

The trough was filled with the particular oil at 30° C. to 40° C., and covered with a dull black lid, and the spectroscope placed in position after the small reflecting prism had been swung aside. From the opposite end a beam of light was transmitted through the oil from a metallic filamented $\frac{1}{2}$ -watt electric bulb of the gas-filled type (50 c.p.), and the slit of the spectroscope was suitably adjusted. As the observations were made in daylight the prism of the instrument was covered with a black cloth.

Diagrams of spectra made from the results obtained have shown that both the limits of visibility and the width of an absorption band, and in some measure its intensity, bear a relation to the horizontal thickness of the oil through which white light is transmitted.

In practice, some difficulty arises in precisely determining the edge of an absorption band, because the absorption becomes less towards the edge, which is therefore not sharply defined, but shaded off to a limit at which absorption is not detectable. Small differences due to this cause, however, are not so great as the differences, in most instances, of the extent of visibility of the spectra of oils of different nature which I have examined.

It would thus appear to be of no use merely to state the width of any absorption bands appearing in the spectrum of an oil, and if the breadth of a band be measured it should be connoted with the thickness of oil through which the light passes before entering the spectroscope. In view, however, of the untrustworthy evidence afforded by such bands too much reliance should not be placed either on their width or their presence or absence.

HOMOGENEOUS LIGHT.—The effect of passing light as nearly as possible homo-

geneous through the various oils was tried by interposing a red glass screen between the source of white light and the oil.

The visibility of the spectrum given by the screen itself ranged from 43.5° in the red to 44.3° in the yellow. It thus filtered out the whole of the violet, indigo, blue, green, and most of the yellow rays from white light, and permitted light very nearly homogeneous to penetrate the oil.

As was probably to be expected, in the case of those oils the spectra of which exceeded in visibility the spectrum of the screen, the spectrum obtained was that of the screen only.

Similarly, in the case of a mixture of two different oils yielding spectra with visibilities differing in extent, the spectrum observed when white light is passed through the mixture is (excluding any absorption bands due to chromogenetic causes in either oil) that of the oil giving the spectrum of the less extensive visibility, provided the limits of visibility at both ends come within the limits of visibility of the spectrum from the oil giving the more extended spectrum. Whether this holds good for an admixture of a very small amount of one oil with another remains yet to be determined.

SPECTROMETRIC CHARACTERISTICS.

| Oil. | Three Inches of Oil used. | | | Six Inches of Oil used. | | |
|-------------------------------|--|---|-----------------------------------|--|---|-----------------------------------|
| | Visibility of Spectrum in the Red ends at— | Visibility of Spectrum in the Blue ends at— | Approximate Extent of Visibility. | Visibility of Spectrum in the Red ends at— | Visibility of Spectrum in the Blue ends at— | Approximate Extent of Visibility. |
| Almond | 43° | 47.3° | 4.3° | 43° | 47° | 4° |
| Arachis | 43.3° | 45.6° | 2.3° | 43.6° | 45.3° | 1.7° |
| Castor (East Indian) | Slightly varies about 43.2° | 45 to 45.3° | 2 to 2.3° | Six inches not suitable for examination | | |
| Coconut | 43.28° | 47.3° | 4.02° | 43.3° | 46.6° | 3.3° |
| Colza (2 inches of oil) | 43.3° | 44.6° | 1.3° | Six inches not suitable for examination | | |
| Cotton seed (English refined) | 43° | 46.6° | 3.6° | 43° | 45.6° | 2.6° |
| Linseed, raw | Slight | 45° | 2.0° | Slight | 44.6° | 1.6° |
| Linseed, boiled | 43.3° | 44.3° | 1.3° | 43° | 44.3° | 1.3° |
| Neatsfoot | 43.3° | 45.64° | 2.34° | 43.6° | 44.34° | About 0.74 , under 1° |
| Olive | Nil | 45.3° | 2.3° | 43.16° | 45.16° | 2° |
| Sesame | 43.16° | 45.6° | 2.46° | 43.3° | 45° | 1.7° |

CONCLUSION.—From the experimental data obtained it seems evident that careful spectrometric observations afford a quick and ready means of identifying a fixed oil, at any rate in the case of those specified.

The above table indicates the spectrometric characteristics of the oils examined,

from which it will be noticed the variations in the extent of visibility are most marked at the blue end of the spectrum, the limits of visibility at the red end not greatly varying.

It will also be seen that the lengths of the visible spectra are mostly different.

DISCUSSION.

Mr. H. C. REYNARD said he would like Mr. Gardner to give some idea of the effect of the age of the seed from which the oil is extracted on the absorption spectrum, as there seemed to be more difference in the absorption spectrum of American "butter oil," prepared from fresh cottonseed, than in that of oil from the kind of seed we are accustomed to get in England. He considered that no amount of refining would give oil, from the latter seed, of so good a colour as the American oil. He feared that as a means of diagnosis of oil the method described by the author was likely to be too much affected by the method of refining and the source of the oil, although, judging by the amount of data given in the paper, probably the writer had already studied this question.

Mr. BOLTON said that, while he was not impressed by spectrometric methods as an analyst's weapon, the readings might prove useful as a manufacturer's method of sorting oils. The data given, however, were most valuable.

Mr. CHAPMAN asked for information as to what the absorption spectrum was really due. He inquired if certain constants were peculiar to certain oils, in which case the test might become of diagnostic value—apart from the other colour, which was, to some extent, accidental. He wondered if the speaker had examined tung oil.

Mr. GARDNER, in his reply, said that Mr. Reynard's point was, perhaps, the weakness of the method. A good deal of cottonseed oil was obtainable from India, the examples dealt with in the paper, however, being imported English refined oils. Undoubtedly the process of refining removed the chromogenetic principle, and colouring matters were rather a cause of absorption bands than otherwise. The colour which remained in the oil was dependent on clarifying, as would be realised on comparison with the figures given (in the charts) for neatsfoot oil. The absorption spectrum bore no relation to the constituents of the oil.



THE SEPARATION OF ALUMINIUM FROM BERYLLIUM.—PART I.

BY HUBERT T. S. BRITTON, B.Sc., F.I.C.

JUDGING from the number and variety of methods of separation of aluminium from beryllium described in the literature, it may be inferred that the problem has been the source of much difficulty. The bulkiness and gelatinous nature of both the aluminium and beryllium hydroxide precipitates render the methods involving them extremely difficult to make quantitative on account of the property possessed by each to adsorb substances from solution.

The following is an epitome of the methods which have been described :

1. Digestion of hydroxides with a concentrated solution of ammonium carbonate, causing beryllium hydroxide to pass into solution. (Vauquelin, *Ann. Chim. Phys.*, 1798, **26**, 155.)

2. Treating aluminium and beryllium hydroxides with a saturated solution of ammonium chloride and boiling until all free ammonia gas has been liberated, beryllium hydroxide alone becoming soluble. (Berzelius *vide* H. Rose. *Handbuch der Analytischen Chemie*, 1851, II., 61.)

3. Decomposition of either sodium or potassium hydroxide solutions of beryllium hydroxide when diluted and boiled for a short time. (Gmelin, *Pogg. Annalen*, 1840, **50**, 175.)

4. Solubility of both beryllium and aluminium hydroxides in either sulphurous acid or in a concentrated solution of ammonium hydroxide saturated with sulphur dioxide. When the solution is boiled to expel sulphur dioxide aluminium hydroxide is precipitated. (Berthier, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 74.) A similar method has been described substituting a solution of sodium thiosulphate, being an adaptation of Chancel's method of estimating aluminium. (*Comptes rend.*, 1858, **46**, 987.)

5. Precipitation of aluminium as basic sulphate by addition of zinc to a solution in sulphuric acid. (Debray, *Ann. Chim. Phys.*, 1855, [iii.], **44**, 1.) This method was claimed by Scheffer (*loc. cit.*, 1859, [iii.], **56**, 112) to be satisfactory, though the digestion with zinc required from two to three days.

6. A method was described by Gibbs in 1864 (*Sill. Amer. J. Sci.*, **37**, 356), in which the oxides were fused with potassium hydrogen fluoride. The fused mass was treated with boiling water containing a little hydrofluoric acid to extract the beryllium as a double fluoride, which crystallized out on cooling.

7 Rössler (*Zeitsch. anal. Chem.*, 1878, **17**, 148) was able to precipitate beryllium as a double ammonium phosphate by the addition of ammonium phosphate in presence of citric acid, but only when the quantity of aluminium present was small.

8. Vincent (*Bull. Soc. Chim.*, 1880, **33**, 157) stated that the salts of beryllium were insoluble in excess of dimethylamine due to the precipitation of beryllium hydroxide, whereas aluminium hydroxide was soluble. C. Renz (*Ber.*, 1903, **36**, 275) applied this fact, and also showed that beryllium hydroxide was precipitated by either methylamine or mono- or di-ethylamine. He gave satisfactory data obtained from an ethylamine separation.

9. Haven's method (*Chem. News.*, 1897, **76**, 111) depends upon the insolubility of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in concentrated hydrochloric acid and ether, saturated with hydrochloric acid gas.

10. Solubility of basic beryllium acetate in chloroform. (Haber and Vau Oordt, *Zeitsch. anorg. Chem.*, 1903, **40**, 465.)

11. Hart (*J. Amer. Chem. Soc.*, 1895, **17**, 604) suggested the use of a strong solution of sodium carbonate, which precipitated the major portion of the aluminium hydroxide. This method was later modified by Parsons and Barnes (*loc. cit.*, 1906, **28**, 1589), who recommended boiling for a half minute with a 10 per cent. solution of sodium bicarbonate.

12. Fusion of BeO and Al_2O_3 with excess of sodium carbonate for two or three

hours, and then extracting the sodium aluminate with water, beryllium oxide remaining unattacked. (Wünder and Wenger, *Zeitsch. anal. Chem.*, 1912, **51**, 470-3.)

13. Method depending upon the volatility of basic beryllium acetate, which Kling and Gelin (*Bull. Soc. Chim.*, 1914, **15**, 205) state can be carried out by distilling the basic acetate of beryllium under reduced pressure, 19 mm. in a current of acetic acid between 160° and 170° C. for four hours, and then for another hour at 250° C. Results within 2 per cent.

Of these, methods Nos. 1, 2, 3, 4, 11 depend upon the peculiarity possessed by beryllium of forming soluble basic salts. This may be explained by the work of Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 864), who found that the hydrogen ion concentration necessary to precipitate aluminium and beryllium hydroxides by means of sodium hydroxide, differed only by a small amount—viz., about 10^{-3} and 10^{-5} respectively. Hence, methods of separation depending upon this difference—e.g., using a solution of sodium thiosulphate, giving hydrogen ions by hydrolysis—will not be likely to be very satisfactory.

It therefore seemed that in the separations depending upon the formation of soluble basic salts of beryllium, sufficient amounts of the reagents must be taken to maintain the necessary hydrogen ion concentration to keep the beryllium hydroxide in solution; in other words, there must be limits of solubility of beryllium hydroxide in solutions of reagents for definite temperatures and concentrations. Such limits have been found in the case of ammonium carbonate, sodium carbonate, and bicarbonate. Knowing the amount of beryllia which a reagent can hold in solution and in which aluminium hydroxide is insoluble, then it would appear at first sight that a method had been found to give a complete separation, if a sufficient quantity of the reagent had been employed. If only the phenomenon of "sorption" by colloidal precipitates could be eliminated or reduced to a minimum, the above methods might be useful.

On account of this, it was thought much more desirable to try to find the conditions necessary for obtaining a quantitative separation of beryllium hydroxide in the form which can be easily washed. The precipitate of beryllium hydroxide obtained by boiling dilute sodium or potassium hydroxide solutions was found to be granular, and when examined microscopically was seen to be composed of small particles, perhaps crystalline, of a little over 1μ in diameter. In this form it could be completely washed, and as was proved by Van Bemmelen ("Die Absorption," *Gesammelte Abhandlungen über Kolloide und Absorption*, 1910, 97) does not adsorb substances from solution.

This method has been investigated by several workers. Vauquelin in 1798 (*Ann. Chim. Phys.*, **26**, 155) first noticed that alkalis dissolved beryllium hydroxide, which was again thrown down on boiling. Gmelin (*Pogg. Annalen*, 1840, **50**, 175) found that, if the alkali solution was not too dilute, the deposition of beryllium hydroxide, after boiling from fifteen to twenty minutes, was complete. Similar conclusions were drawn by Schaffgotsch (*Pogg. Annalen*, 1840, **50**, 183), who also stated that the precipitate was an insoluble salt of potassium, from which the potassium could be removed by washing, rendering the precipitate once again soluble. Weeren (*Pogg. Annalen*, 1854, **92**, 91), Hofmeister (*J. prakt. Chem.*, 1859, **76**, 3), and Joy (*Sill. Amer. J. Sci.*, 1863, **36**, 83-91), all obtained unsatisfactory results. Penfield and

Harper (*Amer. J. Sci.*, 1886, [iii.], **32**, 110) found the method, using sodium hydroxide, to give a good separation when the liquid was boiled for an hour at a dilution of 800 c.c., glass vessels being as suitable as those of platinum. The method was considered best by Zimmermann in 1887 (*Diss.*, Berlin; *Zeitsch. anal. Chem.*, 1888, **27**, 61-63), who stated that quantitative results were only obtainable from potassium hydroxide solutions when boiled for fifteen to twenty minutes in a platinum basin, the dilution for 0.3 gm. BeO not being allowed to exceed 300 c.c. Haber and Van Oordt (*Zeitsch. anorg. Chem.*, 1904, **38**, 377) studied the process from the point of view of the solubility of the "crystalline" hydroxide in various concentrations of sodium hydroxide solution. Some correct separations were obtained by Wünder and Chéladzé in 1911 (*Ann. Chim. analyt.*, **16**, 205), though in the one case where they did not obtain an accurate separation they attributed it to not having used sufficient potassium hydroxide to keep the aluminium hydroxide in solution. They obtained, however, in other instances correct separations when employing less alkali.

This method has proved satisfactory in the hands of several workers, but others have tried it without success. Their failure was probably due to their having employed too much alkali to redissolve the hydroxides or to having unduly prolonged the boiling. An effort has been made to establish the conditions necessary to give correct separations, which will now be described.

EXPERIMENTAL PART.

Pure beryllium sulphate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$) was obtained by treating commercial beryllium nitrate with excess of fairly concentrated sulphuric acid, heating until basic sulphate had dissolved, and then crystallising the salt by pouring the solution into alcohol. The crystals were washed with alcohol and recrystallised from an aqueous solution. An analysis of the beryllium sulphate gave BeO = 14.10 per cent.; SO_3 = 45.21 per cent. Calculated as $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, BeO = 14.16 per cent.; SO_3 = 45.17 per cent.

An exact 0.5 N beryllium sulphate solution and a number of sodium hydroxide solutions, of normalities varying from 0.1 N to 6.5 N, were made up. Ten c.c. of 0.5N beryllium sulphate solution were placed in a beaker, and just sufficient sodium hydroxide solution was run in, drop by drop, to redissolve the precipitated hydroxide, this being indicated by the disappearance of opalescence. The solutions were then diluted to 500-600 c.c. and boiled for forty minutes, the volumes being maintained by occasionally adding water, after which the beryllium hydroxide was immediately filtered off by suction, and washed until no colour was obtained on dropping phenolphthalein on the precipitates. The precipitates were ignited and weighed, and the filtrates tested for presence of beryllium by acidifying with hydrochloric acid and adding ammonium chloride and ammonium hydroxide. The results given on p. 363 were obtained :

In the cases Nos. 1 to 6 the depositions were quantitative. A slight amount of beryllium hydroxide remained in solution in No. 8. A solution of 10 c.c. 0.5 N. BeSO_4 and 41.1 c.c. 1.0 N. NaOH was diluted and boiled, in order to find what deposition was obtained when the ratio of NaOH to BeO was between 8.56 to 1 and 19.76 to 1

(*cf.* Exp. No. 7). The deposition of beryllium hydroxide produced was quantitative; an unweighable precipitate was formed on acidifying the filtrate with hydrochloric acid, adding ammonium chloride and ammonium hydroxide, and allowing the liquid to stand for some time.

TABLE I.

10 c.c. of 0.5 N-BeSO₄ = 2.5 millimols BeSO₄.

| No. | NaOH Solution used. | Number of C.c. NaOH required to Precipitate Be(OH) ₂ and Re-dissolve it. | Millimols NaOH required to keep 2.5 Millimols Be(OH) ₂ in Solution. | Total Volume of Mixture. | Mols. NaOH / Mols. Be(OH) ₂ |
|-----|---------------------|---|--|--------------------------|--|
| 1 | 6.51 N | 2.4 | 10.6 | C.c. 12.4 | 4.24 |
| 2 | 4.0 N | 3.9 | 10.6 | 13.9 | 4.24 |
| 3 | 2.84 N | 6.0 | 11.9 | 16.0 | 4.76 |
| 4 | 2.0 N | 8.5 | 12.0 | 18.5 | 4.80 |
| 5 | 1.25 N | 14.85 | 13.6 | 24.85 | 5.44 |
| 6 | 1.0 N | 26.4 | 21.4 | 36.4 | 8.56 |
| 7 | — | — | 39.1 | — | 15.6 |
| 8 | 0.113 N | 500 (approx.) | 49.4 | 510.0 | 19.76 |

From Table I. it will be observed that the amount of sodium hydroxide required when dilute solutions are used is much greater than for more concentrated solutions of sodium hydroxide. Hence the use of a concentrated sodium hydroxide solution is desirable in order to keep the ratio NaOH/BeO less than 15/1, so that complete deposition will ensue.

The amount of sodium hydroxide required to keep aluminium hydroxide in solution was investigated, and fortunately the quantity required was small.

A 0.5 N-aluminium sulphate solution was made up, pure aluminium sulphate being used. Fifty c.c. of 0.5 N-aluminium sulphate were placed in a beaker and sodium hydroxide solution run in until complete re-solution was just obtained.

TABLE II.

Results : Calculated for 10 c.c. 0.5 N-Al₂(SO₄)₃ = 1.67 millimols Al(OH)₃.

| No. | NaOH used. | Number of C.c. of NaOH required to Precipitate and Re-dissolve Al(OH) ₃ . | Millimols NaOH required to Dissolve Precipitated Al(OH) ₃ . | Mols. NaOH ₃ / Mols. Al(OH) ₃ |
|-----|------------|--|--|---|
| 1 | 1.0 N | 6.90 | 1.90 | 1.14 |
| 2 | 6.51 N | 1.05 | 1.84 | 1.10 |
| 3 | 5.88 N | 1.17 | 1.88 | 1.12 |

The amount of sodium hydroxide required is, therefore, only slightly more than that required for the quantitative formation of NaAlO₂ (*cf.* Heyrovsky, *J. Chem.*

Soc., 1920, **117**, 1013). Solutions of aluminium hydroxide (0.4259 grms. Al_2O_3) in the minimum amount of sodium hydroxide were diluted in one case to 400 c.c., in another to 600 c.c., and in a third to 800 c.c. These were boiled, but in no instance did any deposition of aluminium hydroxide occur in less than two hours, the largest amount being from the 800 c.c. dilution, which amounted to about 4 per cent. after three hours. Diluted solutions were allowed to stand overnight, and in each case slight depositions were observed.

It has been noticed that when decomposition of the aluminate solution begins, causing a deposit (in what has been described as the crystalline form) on the walls of the beaker, the decomposition thereafter becomes more rapid. Slade and Polack (*Trans. Faraday Soc.*, 1914, **10**, 150) also noticed that the deposition on surfaces such as platinum, being rougher than glass, took place somewhat more quickly. It is therefore conceivable that there may be a chance of aluminium hydroxide depositing more quickly than usual on glass, on the deposited beryllium hydroxide if allowed to accumulate on the side of the beaker. In one separation, in which boiling had been continued for an hour, a slight quantity of alumina was deposited with the beryllium hydroxide, comprising about 2 per cent. of the total precipitate. This happened to be a case where beryllium hydroxide had been allowed to deposit somewhat heavily on the beaker, especially round the edge of the surface of the solution.

The amounts deposited during forty minutes' boiling in a dilution of 500 c.c. have proved negligible, as the following results of separations show :

TABLE III.

| No. | Grms. BeO. | | Grms. Al_2O_3 . | | Total NaOH required for Precipitation and Re-solution. | |
|-----|------------|--------|---------------------------------|--------|--|---------|
| | Taken. | Found. | Taken. | Found. | c.c. | Normal. |
| 1 | 0.2067 | 0.2065 | 0.0600 | 0.0603 | 9.75 | 5.88 |
| 2 | 0.1255 | 0.1258 | 0.1703 | 0.1700 | 7.45 | 6.51 |
| 3 | 0.1255 | 0.1259 | 0.4207 | 0.4210 | 11.40 | 6.51 |
| 4 | 0.0665 | 0.0665 | 0.2491 | 0.2490 | 7.05 | 5.88 |
| 5 | 0.0653 | 0.0658 | 0.2557 | 0.2550 | 6.90 | 5.88 |
| 6 | 0.0262 | 0.0263 | 0.2552 | 0.2554 | 5.80 | 5.88 |
| 7 | 0.0137 | 0.0135 | 0.2547 | 0.2550 | 4.95 | 5.88 |

These mixtures were made up by taking weighed amounts of pure beryllium sulphate and aluminium sulphate. They were dissolved in about 30 c.c. of distilled water, and a concentrated solution of sodium hydroxide added in just sufficient quantity to cause re-solution of the precipitated hydroxides. The clear solution was then diluted to approximately 500 c.c. and boiled for forty minutes, the volume being kept constant. The precipitate was filtered off and washed until free from sodium hydroxide, and finally ignited and weighed.

After the removal of the beryllium hydroxide, the filtrate and washings were in

each case boiled for about half an hour to ascertain whether either the deposition of beryllium hydroxide appeared complete, or if the aluminate solution began to decompose. In every separation there was no deposition, proving that there is a distinct break between the total decomposition of the beryllate solution and the beginning of decomposition of the aluminate solution.

The aluminium oxide was estimated by acidifying the solution with hydrochloric acid and precipitating the aluminium with ammonium chloride and ammonium hydroxide. The aluminium hydroxide precipitate was freed from any adsorbed sodium chloride by igniting the unwashed precipitate in a platinum crucible and extracting it with water containing ammonium chloride and ammonium hydroxide. When washed, the precipitate was ignited and estimated.

From the data given it will be seen that the use of the method is quite general, no matter what ratio of beryllium to aluminium may be present. It was feared that the method would not be satisfactory when the amount of alumina present was great as compared with the amount of beryllia, on account of the amount of sodium hydroxide that might be necessary. The following table is interesting, inasmuch as it shows that the amounts of sodium hydroxide required in the foregoing analyses to get the beryllium hydroxide into solution, after having deducted the amount of sodium hydroxide required by the formula NaAlO_2 , all lie within the amounts given in the preliminary experiments. In the analysis of mixture No. 7, where the amount of BeO is small and that of Al_2O_3 is large, it so happens that the ratio of mols. NaOH to mols. BeO is as 14.8 to 1, and therefore just falls within the limits for the quantitative decomposition of beryllate solutions.

TABLE IV.

| No. | Millimols. | | | | | | Mols. NaOH Mols. Be(OH)_2 |
|-----|--|---------------------|---------------------|-----------------------------------|--|--|--|
| | NaOH required for Precipitation and Re-solution. | Be(OH)_2 . | Al(OH)_3 . | NaOH to Dissolve both Hydroxides. | NaOH converted into NaAlO_2 . | NaOH required to keep Be(OH)_2 in Solution. | |
| 1 | 57.33 | 8.24 | 1.17 | 37.33 | 1.17 | 36.16 | 4.4 |
| 2 | 48.50 | 5.00 | 3.33 | 28.50 | 3.33 | 25.17 | 5.0 |
| 3 | 74.21 | 5.00 | 8.23 | 39.51 | 8.23 | 31.28 | 6.3 |
| 4 | 41.45 | 2.65 | 4.88 | 21.52 | 4.88 | 16.64 | 6.3 |
| 5 | 40.57 | 2.60 | 5.00 | 20.35 | 5.00 | 15.35 | 5.9 |
| 6 | 34.10 | 1.04 | 4.99 | 17.04 | 4.99 | 12.05 | 11.6 |
| 7 | 29.11 | 0.545 | 4.98 | 13.07 | 4.98 | 8.09 | 14.8 |

CONCLUSIONS.

The conditions necessary to render quantitative the method of separation of aluminium from beryllium, depending upon the hydrolytic decomposition of beryllate solutions, have been investigated. They are: 1. Solutions which contain not more than about 0.3 grms. of BeO and 0.4 grms. of Al_2O_3 should be evaporated to about 25 c.c., and brought to the temperature of the room, after which a concentrated

solution of sodium hydroxide—*e.g.*, 6 N-NaOH—is cautiously added until the precipitated hydroxides are just dissolved. [N.B.—Addition of too much sodium hydroxide will produce a slower and incomplete deposition of beryllium hydroxide.]

2. A suitable dilution to produce a complete deposition of beryllium hydroxide after forty minutes' boiling is 500 c.c. Prolonged boiling may cause the deposition of some aluminium hydroxide.

3. The beryllium hydroxide must be filtered from the boiling solution immediately, as the aluminate solution, if allowed to stand for any length of time, will slowly decompose; and, further, there is a tendency for a little beryllium hydroxide to re-dissolve.

The author desires to express his thanks to Professor A. J. Allmand for the interest he has taken in this work.

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NOTES.

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

THE COMPOSITION OF LOCUST BEAN SEEDS.

Smetham (*J. Roy. Lancs. Agr. Soc.*, 1909) gives three analyses of locust beans, and, from the composition of these samples, it is to be presumed that the whole bean is included; there is, however, on the market a product of locust beans, the analyses of which differ materially from those recorded by Smetham, as will be seen from the following percentage figures:

| | A. | B. | C. |
|-----------------------|-------|-------|-------|
| Water | 13·2 | 12·3 | 12·4 |
| Oil | 1·8 | 0·8 | 1·4 |
| Proteins | 14·6 | 7·1 | 23·0 |
| Carbohydrates | 58·6 | 75·0 | 45·2 |
| Fibre | 9·0 | 3·3 | 13·4 |
| Mineral matter | 2·8 | 1·5 | 4·6 |
| | 100·0 | 100·0 | 100·0 |
| Food units | 100 | 95 | 106 |

A is the whole kernel; B is the split kernel, from which the husk has been removed; and C is the "refuse" left after the removal of B. There is no question that these are anything but the genuine product of the locust bean, and are sold as such for feeding cattle.

NOTE ON COLOURING OF THE MICROSCOPE FIELD.

It frequently happens in the examination of crystals—*e.g.*, sugar in foodstuffs—mounted in the ordinary colourless media (cedar-wood oil) that a clear definition is not obtained. If, however, the microscope field be coloured with a suitable colouring matter which does not stain the crystals, a much sharper contrast between the colourless crystal and the surrounding field is obtained. As a result the shape and size of the crystal can be more clearly seen.

In practice it is found that the deep red oil obtained by an oil extraction of alkanet root gives the best results, and the method is particularly applicable to the measurement of the size of sugar crystals in products where other bodies than sugar are present.

The method of application is exactly the same as with other mounting media, the cover-glass being pressed well down without crushing the crystals.

The oil is readily obtained by extracting (in the cold) 100 grms. of finely ground dried alkanet root with about 200 c.c. of cotton-seed or cedar-wood oil for two days, with occasional stirring, and then filtering the extract through two filter papers on a Büchner filter. A further extraction of the ground root with another 100 c.c. of oil, and the addition of the filtrate from this to the first filtrate, gives a red-coloured oil of suitable intensity of colour. Other oil-soluble dyes may be used in place of the above, but alkanet is found very satisfactory. Also, cotton-seed oil is preferable to cedar-wood oil, as in the case of the latter the colour rapidly fades.

The method should be applicable to the examination of any colourless crystals insoluble in the oil.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Detection of Manioc and Rice Flours. L. Desvergnès. (*Ann. Chim. Anal.*, 1921, 3, 205-206.) Ten grms. of the flour are heated in a 200-c.c. flask beneath a reflux condenser for five minutes with 45 c.c. of alcohol (95 per cent.) and 5 c.c. of hydrochloric acid (22 per cent.); the liquid is cooled and filtered, and the colour observed. The following results were obtained with various flours: Oat, straw-yellow colour; wheat, clear rose-yellow tint; maize (yellow), bright yellow colour; manioc, cherry-red colour; barley, clear straw-yellow tint; rice, deep rose colour; rye, yellowish rose colour. With a mixture of pure wheat flour with 10 per cent. of manioc a rosy tint was obtained, but with a mixture of wheat-offal and manioc the strong yellow-brown colour produced by the wheat-offal masked the rose tint. This difficulty was obviated by adding 50 parts of petroleum spirit and 25 parts of water per 100 parts of the alcoholic solution; the upper layer of petroleum spirit then became yellow-brown, and the lower layer (dilute alcohol) a more or less pronounced rose colour.

R. G. P.

Use of Indicators to Determine the Reaction of Whey. Y. Okuda and H. F. Zoller. (*J. Ind. Eng. Chem.*, 1921, 13, 517.) Methyl-red cannot be relied upon to give an accurate indication of the reaction of whey in the region of P_H 4 to 5.3, and it is doubtful if any indicator which covers this region could be employed because of the great protein error. W. P. S.

Estimation of Dextrose, Lævulose, Sucrose and Dextrin in Admixture. A. Behre. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, 41, 226-230.) When a mixture of the sugars is treated with an excess of iodine and sodium hydroxide solutions, as in the method proposed by Willstatter and Schudel (*ANALYST*, 1918, 43, 416), the dextrose alone is oxidised to gluconic acid, whilst the other sugars are not affected; the amount of iodine required for the oxidation is a direct measure of the quantity of dextrose present. If the estimation be repeated after the mixture of sugars has been inverted by heating with hydrochloric acid under the usual conditions, the additional quantity of dextrose found is that derived from the sucrose, and the amount of this sugar is thus ascertained. To estimate the lævulose, the solution remaining after the oxidation of the dextrose with iodine is treated with lead acetate to precipitate iodides and gluconic acid, and the quantity of lævulose then found by determining the cupric-reducing value of the solution. The method may be applied to the estimation of dextrose and dextrin in commercial starch syrup; the increased amount of dextrose found after the sample has been inverted by heating for three hours with hydrochloric acid is that formed by the hydrolysis of the dextrin. If lævulose be also present, it is decomposed by the prolonged acid treatment, and it is necessary to remove the products of decomposition by means of lead acetate before the dextrose is estimated iodimetrically. W. P. S.

Polarimetric Estimation of Mannitol. M. J. Badreau. (*J. Pharm. Chim.*, 1921, 24, 12-19.) The slight negative rotation of mannitol in aqueous solution is changed to a pronounced positive rotation by the action of arsenious acid in alkaline solution. The value increases with the quantity of arsenious acid, and has a maximum of $\alpha_D = +46^\circ 53'$ when the ratio $\frac{As_2O_3}{mannitol} \cong 17.5$. For the estimation of mannitol in solution, 20 c.c. are treated with 30 c.c. of a solution containing 198 grms. of As_2O_3 and 132.5 grms. of Na_2CO_3 per litre, and the mixture is filtered and polarised. The amount of mannitol in the 20 c.c. is then obtained by the formula $\alpha_D = \frac{\alpha V}{Lx}$ where $\alpha_D = 46^\circ 53'$; α is the observed rotation, $V = 50$, and $L =$ length of the tube in dm. Should the 20 c.c. contain more than 0.339 gm. of mannitol, the original solution must be diluted and examined afresh so that the ratio of As_2O_3 to mannitol may be not less than 17.5 : 1. The temperature should be between 16° and 21° C. Alcohol interferes with the estimation and must be removed. Glycerol diminishes the action of the arsenic, but may be neglected, provided that the weight of glycerol in the volume of liquid examined does not exceed the weight of arsenious acid added. If an unknown quantity of glycerol be present, its effect may be eliminated by polarimetrically examining the solution at

successively increased dilutions, when the amount of mannitol indicated will increase to a maximum and constant value which is the true content. Mannitol cannot be estimated by the polarimeter in the presence of the following "poly-ols," which are acted upon by arsenic: Quercitol, *d*- and *l*-inositol, erythritol, *d*- and *l*-arabinol, hexols and heptols; but aldoses, ketoses, saccharoses, and polysaccharoses are unaffected, and so do not interfere with the estimation. Tartaric and malic acids are acted upon, and must be removed by lead acetate and subsequent treatment with hydrogen sulphide. Mixtures containing optically active substances and mannitol may be analysed by diluting one portion with water and another with the arsenical solution; the above formula is then applied to the difference between the polarimeter readings, which gives the rotation due to mannitol under the influence of arsenic. This procedure is applied to the estimation of mannitol in manna. For the estimation in manna wine, the alcohol is removed by evaporation, the residue is diluted to its initial volume with water, treated with lead acetate, sodium carbonate added to remove the excess of lead, and the solution decolourised with animal charcoal. In the case of mushrooms, the mannitol may be estimated by repeated extraction with boiling water and treatment of the mixed extracts with lead acetate, hydrogen sulphide, and animal charcoal; two polarimetric readings are then taken, one before and one after treatment with the arsenical solution.

H. E. C.

Manna and the Extraction of Mannitol. G. Scarlata. (*Giorn. Chim. Ind. Appl.*, 1921, 3, 254-255.)—The author describes the sources of the various commercial qualities of manna, and gives the composition of the latter. In the Ruspini method of extracting mannitol from manna, this is first extracted with water, but application of this method to manna containing not less than 15 per cent. of impurities, mostly soil, did not permit of the preparation of pure mannitol in cones. This manna was, therefore, uniformly moistened with about 15 per cent. of water, and, after twenty-four hours, subjected to a high pressure; the manna molasses expressed consists of a dense, reddish syrup, with a green fluorescence, and finds several industrial applications. The pressed cakes were dissolved in the minimum quantity of hot water, acidified with oxalic acid to precipitate colloidal clay, the solution being freed from scum, leaves, bark, etc., by skimming, and left to cool in a wooden crystallising vat. The upper layer of crystallised mannitol thus formed was separated from the lower one of soil, and, after centrifuging, dissolved in hot water and defecated with alum and lime; after filtration through felt and subsequent concentration and cooling, pure and almost colourless crystals of mannitol were obtained. Dry distillation of manna *in vacuo* at as low a temperature as possible yields a dense liquid distillate, which apparently contains the mannitol anhydrides, mannide, and mannitan, these yielding mannitol on hydrolysis. This method may serve as a means of separating mannitol from manna.

T. H. P.

Estimation of Methyl Alcohol and Ethyl Alcohol in Spirits, Medicines, Cosmetics, etc., by means of the Zeiss Immersion Refractometer. W. Lange and G. Reif. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, 41, 216-226.)—A definite

volume of the sample is rendered slightly alkaline and distilled through an efficient fractionating column; when the temperature of the vapours reaches 90° C. the distillation is stopped, the volume of the distillate is noted, and its specific gravity is determined. The approximate alcoholic strength is found by reference to tables, and water is added to the distillate in quantity sufficient to make the alcoholic strength exactly 50 per cent. by volume. At this concentration the specific gravity at 15° C. of methyl alcohol is the same as that of ethyl alcohol, namely 0.9346. The specific gravity should be re-determined after the dilution, and a further quantity of water added, if necessary. The refraction of the solution is then determined by means of the immersion refractometer. A 50 per cent. aqueous solution of methyl alcohol gives a scale reading of 40.2°, whilst a 50 per cent. solution of ethyl alcohol gives a reading of 85.6°. Tables are given in the original showing the scale readings of 50 per cent. alcoholic solutions containing from 0 to 50 per cent. of methyl alcohol.

W. P. S.

Detection of Tartaric Acid in Wines. L. Mathieu. (*Bull. Assoc. Chim. Sucr.*, 1921, **38**, 352-354.)—About 20 c.c. of the wine are shaken with 20 c.c. of amyl alcohol; the alcoholic layer is separated and shaken with an equal volume of water; the aqueous layer is then drawn off, evaporated to dryness, the residue is dissolved in 5 c.c. of water, and the solution treated with 1 drop of calcium chloride solution (150 grms. of crystallised calcium chloride and 40 grms. of ammonium chloride per litre) and 2 c.c. of *l*-ammonium tartrate solution (20 grms. of the salt per litre of dilute alcohol). A precipitate of calcium racemate forms immediately if the wines contain not less than 0.5 grm. of free tartaric acid per litre.

W. P. S.

Detection of Saccharin in Wine. C. von der Heide and W. Lohmann. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **41**, 230-236.)—Five hundred c.c. of the wine are evaporated to a volume of about 250 c.c. to remove the alcohol, the residual solution is cooled, acidified with 10 c.c. of dilute sulphuric acid, and extracted thoroughly with ether. The ethereal solution is washed with water, the greater part of the ether is then distilled off and recovered, and the remainder is removed by evaporating the solution in a porcelain basin. The dry residue thus obtained is dissolved in a small quantity of very dilute sodium hydroxide solution; the solution is heated on a water-bath, and small quantities of 5 per cent. potassium permanganate solution are added from time to time, until a persistent red coloration is obtained; the solution is then acidified, and again oxidised by the addition of permanganate solution. Sulphurous acid is now added to destroy the excess of permanganate, the solution is evaporated to about 25 c.c., cooled, and extracted with three successive quantities of 10 c.c. of ether; the united ethereal extracts are washed with water and evaporated, and the residue moistened with 3 c.c. of water and again evaporated. This treatment with water and evaporation is repeated many times during one hour. Free benzoic acid is thus removed completely. The residue obtained finally is dissolved in water and a drop of the solution is tasted; a pronounced sweet taste indicates the presence of saccharin, and this indication may be confirmed by evapor-

ating the solution, fusing the residue with sodium hydroxide, and identifying the resulting salicylic acid by the usual tests.

W. P. S.

Action of Phosgene on Ricinolein. A. Piutti and A. Curzio. (*Giorn. Chim. Ind. Appl.*, 1921, 3, 242-244.)—When a current of phosgene is passed through castor oil heated at 100° C., a trichlorocarbonic product is obtained which, when freed from excess of phosgene by repeatedly shaking with hot water until the latter fails to assume an acid reaction, is found to contain on the average 9.03 per cent. (8.96 to 9.15) of chlorine. The products obtained in the same way from olive, arachis, almond, and sesamé oils, which are free from hydroxyl groups, contain only from 0.08 to 0.18 per cent. of chlorine, and the method is suggested as a means of detecting adulteration of castor oil. To estimate the chlorine in the chlorinated oil, 0.2 to 0.5 gm. of the latter is mixed in a platinum crucible in the shape of a short test-tube, with pure dry sodium carbonate, and the crucible then filled with the carbonate and heated, at first gently and then more strongly, to incipient fusion of the lower layer. When cold, the contents of the crucible are dissolved in dilute nitric acid and the chlorine estimated volumetrically by the Volhard method.

T. H. P.

Detection of Beef Fat in Lard by Bömer's Method. Vitoux and C. F. Muttelet. (*Ann. Chim. Anal.*, 1921, 3, 208-215.)—The melting-points of the glycerides (G) from 38 samples of lard of authenticated origin, determined by the method previously described (*ANALYST*, 1921, 94) were as follows: From 64° to 65.2° C., 28 samples; 63° to 63.8° C., 6 samples; 62° to 62.8° C., 3 samples; 61.4° C., 1 sample with abnormal refractive index (oleorefractometer degree at 45° C., -16.2°). The differences between the melting-point of the glycerides (G) and the melting-point of the fatty acids (A) were as follows: From 5° to 7.5° C., 31 samples; 4.8° C., 6 samples; and 4.6° C., 1 sample. In the case of five samples of beef fat the melting-points of the glycerides (G) varied from 54° to 58° C., and ($G - A$) varied from 2.0 to 4.0° C. It is suggested that the value $2G - A$ should be employed as a basis of comparison of results rather than that recommended by Bömer, viz.: $G + 2(G - A)$. In the case of the samples of lard examined, $2G - A$ was equal to or greater than 68° C., whilst for the five samples of beef fat it varied from 59.6° to 62.6° C.

R. G. P.

Sheep-foot and Ox-foot Oils. A. Bruno. (*Ann. Falsific.*, 1921, 14, 137-139.) Specimens of the oils prepared in the laboratory had the following physical and chemical characters: *Sheep-foot Oil*—Sp. gr. at 15° C., 0.917; $[n]_D^{20}$ C., 1.46805; iodine value, 84.0; saponification value, 194; and free fatty acids (as oleic acid), 0.34 per cent. *Ox-foot Oil*—Sp. gr. at 15° C., 0.9169; $[n]_D^{20}$ C., 1.4675; iodine value, 75.3; saponification value, 194; and free fatty acids (as oleic acid), 0.87 per cent. Both oils yielded a pink coloration with Bellier's resorcinol reagent.

W. P. S.

Calcium Content of White-of-Egg. H. Kreis and J. Studinger. (*Ann. Falsific.*, 1921, **14**, 148-151.)—The quantity of calcium in fresh white-of-egg varies considerably, the ash containing from 0.59 to 4.25 per cent. of its weight of calcium oxide. There is no appreciable increase in the calcium content when eggs are immersed in lime-water for several months, and the original weight of the eggs is not altered. The calcium content does not, therefore, afford any evidence as to whether or not an egg has been preserved in lime-water. The membrane enclosing the yolk is, however, rendered very fragile when an egg is immersed in lime-water, even for a relatively short period. W. P. S.

Estimation of Lecithin. J. L. B. van der Marek. (*Pharm. Weekblad*, 1921, **58**, 989-992.)—In Hager's method of estimation (*Pharmazentische Praxis*) the lecithin is decomposed by boiling with nitric and sulphuric acids, and the phosphoric acid precipitated with ammonium molybdate. The precipitate is washed, suspended in water, and dissolved in $\frac{N}{2}$ alkali hydroxide solution, an excess of 5 to 6 c.c. being added, and the solution is boiled until all ammonia is expelled, and then titrated with $\frac{N}{2}$ hydrochloric acid. Each c.c. of $\frac{N}{2}$ alkali corresponds (according to Hager) with 1.268 mgrms. of P_2O_5 . In the author's experience this method is tedious and quite unreliable. The phosphoric acid may be estimated directly in the residue obtained after removal of organic matter by a mixture of nitric and sulphuric acids. The acid is first neutralised with alkali, and ammonium chloride and ammonia are added to the solution until a precipitate forms, which is then dissolved in dilute hydrochloric acid. Magnesia mixture is added, and the solution is treated with ammonia at boiling temperature. It is not possible, however, to determine the amount of lecithin in a sample from its phosphoric anhydride content, as the formula $C_{42}H_{81}NPO_9$ is doubtful. W. J. W.

Volatile Oil from the Leaves of *Ocimum Gratissimum*, Linn. O. D. Roberts. (*J. Soc. Chem. Ind.*, 1921, **40**, 164-165r.)—The leaves of this plant yield on distillation about 0.1 per cent. of volatile oil, having an odour similar to that of cloves, and the following constants: Sp. gr. (15°/15° C.), 0.995-0.996, α_D , -12.7° to -14.0°, $[n]_D^{20} = 1.526-1.532$. The approximate composition of the oils is: Terpenes (chiefly ocimene), 16.0; phenols (eugenol), 55.0; phenol ethers (as methyl chavicol), 5.6; alcohols (probably linalool), 13.0; esters (as $C_{10}H_{17}OH$), 0.6; and residue, 9.8 per cent. The volatile oil from *Ocimum basilicum* appears to be somewhat similar to that described above, having: Sp. gr. (26° C.), 0.890-0.940, α_D , -11.25° to -18°, and containing 30 to 46 per cent. eugenol, and the terpene ocimene. H. E. C.

Estimation of Glycyrrhizin in Liquorice Root. P. A. Houseman. (*Amer. J. Pharm.*, 1921, **93**, 481-495.)—The author discusses the conclusions arrived at by Linz in his experimental examination of twenty-seven methods for the estimation of glycyrrhizin in liquorice, and also criticises the method devised by Linz (*Arch. der Pharm.*, 1916, **254**, 65 and 204). A detailed description is given of experimental work upon which the following method was based: The root is ground to pass a 20-mesh sieve, and dried at 50° C. to a moisture content of less than 2 per

cent. Three grms. of the powder are treated in an extraction apparatus with 50 c. c. of ether, dried, and transferred to a 100-c.c. centrifuge tube, to which 75 c. c. of 75 per cent. alcohol are added. After frequent stirring, followed by standing overnight, the tube is whirled in the centrifuge, the clear liquid is poured off, and the alcoholic extraction of the residue twice repeated. The mixed extracts are evaporated to dryness, dissolved in 10 c. c. of water, filtered, diluted to 20 c. c., and precipitated by the addition of 3 c. c. of 10 per cent. sulphuric acid. The residue is washed with two 5-c.c. portions of ice-cold water saturated with ether, and dissolved in 30 c. c. of warm 95 per cent. alcohol. The acid solution and washings are mixed and neutralised by the addition of ammonia, evaporated to about 5 c. c., and treated with 2 c. c. of 10 per cent. sulphuric acid, and the precipitate washed with iced ether-water as above. This precipitate is dissolved in 10 c. c. of warm 95 per cent. alcohol, filtered, and added to the alcoholic solution of the first residue. To the mixed solutions 2 drops of 5 per cent. ammonia are added, the solution evaporated to dryness, and the residue dried at 100° C. and weighed. The method yields results considerably higher than do previous methods, and the glycyrrhizin obtained is light in colour, intensely sweet, and free from resins and bitter substances. The method adopted by the author for the estimation of glycyrrhizin in liquorice extract is similar to the above. The estimations, which may be made upon liquorice root, should include moisture, total ash, ash insoluble in hydrochloric acid, resins, glycyrrhizin, sugars, crude fibre, and the percentage of material passing sieves of standard mesh.

T. J. W.

Estimation of Yohimbine in Yohimba Bark. A. Schomer. (*Pharm. Zentr.-h.*, 1921, **62**, 169-171; *J. Chem. Soc.*, 1921, **120**, ii., 360.)—Fifteen grms. of powdered bark and 150 grms. of ether are shaken together for ten minutes, 10 grms. of sodium hydroxide solution (15 per cent.) are then added, and after shaking and allowing to stand for one hour, 100 grms. of the ethereal solution are shaken and extracted with successive quantities of hydrochloric acid (1 per cent.). The acid extract is shaken with chloroform (25 c. c.), and, after separation of chloroform, is made alkaline with sodium carbonate and extracted with chloroform. The crude alkaloidal residue left on evaporating the chloroform is dissolved in a small quantity of alcohol containing a few drops of hydrochloric acid, the alcohol is evaporated, 5 c. c. of ether are added, and also evaporated. The residue is then warmed with 50 drops of alcohol, the mixture evaporated almost to dryness, and the crystalline residue treated with 50 grms. of chloroform and cooled to 0° C. The crystals are collected, dried at 100° C., and weighed.

R. G. P.

Apomorphine Hydrochloride. D. B. Dott. (*Pharm. J.*, 1921, **107**, 102.)—Examination of various samples of this salt showed the water of crystallisation to lie between one-half and one mol. per mol. of the anhydrous salt. By drying nine samples in air and determining the moisture immediately the salt was observed to be apparently dry, the mean result obtained was 4.27 per cent., corresponding to three mols. of water combined with four mols. of the salt. Apomorphine hydrochloride gradually becomes anhydrous over sulphuric acid in a desiccator, and more

rapidly when heated on a water-bath. A slight loss of hydrochloric acid occurs on heating the compound at 100° C. for a protracted period, and at 140° C. a further loss occurs, together with slight oxidation.

T. J. W.

Assay of Aconite. A. R. L. Dohme. (*Amer. J. Pharm.*, 1921, **93**, 426-429.)—

The mixed ether-soluble alkaloids obtained in the chemical examination of aconite and its preparations consist of aconitine, benzoyl-aconine and aconine; the two latter do not possess the therapeutical properties of aconitine, and as it is not possible to separate them quantitatively by chemical means in such a way that the amount of aconitine may be estimated, the chemical method of analysis is useless for determining the quality of aconite. Aconitine is about 300 times as toxic as benzoyl-aconine and 3,000 times as toxic as aconine, and a physiological method proposed is based on this fact. In the case of the fluid extract, 1 c.c. is diluted to 10 c.c. with 50 per cent. alcohol; the smallest quantity of this solution which, when diluted to 1.5 c.c. with normal salt solution and injected into the subcutaneous tissues of a 400 gm. guinea-pig, will kill within twenty-four hours, is taken as the lethal dose. With aconitine, this dose is about 0.0000005 gm. per gm. of guinea-pig.

W. P. S.

Podophyllum Ash Standards. E. L. Newcombe, C. H. Rogers and C. W. Folkstad. (*Amer. J. Pharm.*, 1921, **93**, 429-432).—Commercial samples of podophyllum frequently yield more than 3 per cent. of ash. Plump starchy roots and rhizomes usually yield less than 3 per cent. of ash, whilst shrivelled rhizomes and roots give between 4 and 5 per cent. The amount of ash is increased if the material is not cleaned properly. One sample of commercial podophyllum powder examined contained 8.88 per cent. of ash and 5.95 per cent. of ash insoluble in hydrochloric acid.

W. P. S.

Hydrastis (Golden Seal).—In the proposed standard (*ANALYST*, 1921, 143), for "acid-soluble ash" read "acid-insoluble ash."

Estimation of Formaldehyde and Paraformaldehyde in Tablets. N. Evers and C. M. Caines. (*Pharm. J.*, 1921, **106**, 470).—In the method proposed the sample is heated with water to convert paraformaldehyde into formaldehyde, and the latter is then estimated colorimetrically by means of Schiff's reagent. A tablet is weighed and boiled with 200 c.c. of water under a reflux condenser for thirty minutes; after the solution has cooled, the condenser is washed down with water, and the solution is diluted to 250 c.c., and filtered. A standard solution is prepared by diluting 1 c.c. of 38 per cent. formaldehyde solution to 1 litre; a series of standards is then prepared in ten test-tubes, quantities of 0.1 c.c. to 1.0 c.c. of the formaldehyde solution being taken, and each diluted to 10 c.c. Ten c.c. of the filtered tablet solution are placed in another test-tube, and to each tube is added 2 c.c. of Schiff's reagent. The colorations obtained are compared after the lapse of three minutes. The Schiff's reagent is prepared by dissolving 0.2 gm. of magenta in 10 c.c. of water, saturating the solution with sulphur dioxide, and, after twenty-four hours, diluting it

to 200 c.c. Low results were obtained when the tablets were steam-distilled and the formaldehyde estimated iodimetrically in the distillate.

W. P. S.

Approximate Estimation of Commercial Cresol in Lysol. C. J. Jordan and F. Southerden. (*Pharm. J.*, 1921, **106**, 479-480.)—Products of somewhat varied composition are sold under the name "lysol," but most of them consist essentially of a strong solution of castor oil or linseed oil soap incorporated with commercial cresol. To estimate the amount of cresol present 60 grms. of the sample are acidified with 30 c.c. of dilute sulphuric acid and steam-distilled until the distillate no longer gives a blue coloration with ferric chloride. The whole distillate is shaken thoroughly, but not too violently, so as to ensure saturation of the aqueous layer, and then set aside for a few hours. The volume of the cresol layer multiplied by 1.04 and added to one-fiftieth of the volume of the aqueous layer gives the weight of cresol in the portion of the sample taken. The method yielded trustworthy results in the case of mixtures containing known amounts of cresol. It is generally agreed that "lysol" should contain 50 per cent. of cresol, but analyses of ten different brands showed that, in some cases, the cresol content was about 40 per cent., and in one sample 35 per cent.

W. P. S.

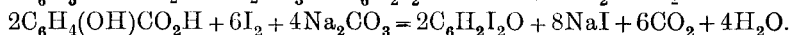
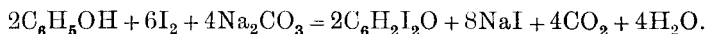
ORGANIC ANALYSIS.

Denigès' Test for the Detection and Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol. R. M. Chapin. (*J. Ind. Eng. Chem.*, 1921, **13**, 543-545.)—Denigès' method for the detection of methyl alcohol (oxidation with permanganate and detection of the resulting formaldehyde by Schiff's reagent) is modified, as described below, in order to increase its sensitiveness and to avoid the development of false reactions. The solution to be tested is diluted until it contains 5 per cent. of total alcohols; 5 c.c. of this solution are then mixed with 0.3 c.c. of 85 per cent. phosphoric acid, and 2 c.c. of 3 per cent. potassium permanganate solution are added. When the permanganate is decomposed completely (about ten minutes), 1 c.c. of 10 per cent. oxalic solution is added, followed, after two minutes, by 1 c.c. of concentrated sulphuric acid and 5 c.c. of Schiff's reagent. If a blue or violet coloration does not appear after ten minutes (any coloration due to acetaldehyde will have disappeared in this time) there is present less than 0.2 per cent. of methyl alcohol in the total alcohol. To estimate methyl alcohol in ethyl alcohol the procedure is as follows: The solution under examination is diluted so that it contains 1 per cent. of total alcohols (solution *A*); 10 c.c. of this solution are mixed with 10 c.c. of 4 per cent. (by vol.) ethyl alcohol solution and diluted to 50 c.c. (solution *B*), and 10 c.c. of solution *B* are similarly mixed with 10 c.c. of 4 per cent. ethyl alcohol and diluted to 50 c.c. (solution *C*). Four c.c. of these three solutions are placed in separate 50 c.c. Nessler cylinders, and in a series of other cylinders are prepared a number of standards containing respectively 1, 2, and 3 c.c. of a 0.04 per cent. methyl alcohol solution; to each of the standards is added 1 c.c. of 4 per cent. ethyl alcohol and water sufficient to make the volume 4 c.c. Each of the six solutions is then treated with 1 c.c. of dilute phosphoric acid (1 vol. of 85 per cent. acid to 4 vols. of water), and 2 c.c. of 3 per cent. potassium permanganate solution; after

thirty minutes, 1 c.c. of 10 per cent. oxalic acid solution is added to each, followed, after about two minutes, by 1 c.c. of concentrated sulphuric acid and 5 c.c. of Schiff's reagent. The contents of the tubes are mixed thoroughly after each of the additions. The colorations obtained are compared after the lapse of one hour. The alcohol solution to be tested should contain alcohols only; many substances, if present, may be removed by distillation, if necessary, with the addition of alkali or acid; formaldehyde and terpenes may be eliminated by treatment with sodium hydroxide and silver nitrate, followed by distillation. Higher alcohols and acetone do not appear to interfere with the test. The Schiff's reagent is prepared by dissolving 0.2 gm. of magenta in 20 c.c. of water, adding 2 grms. of anhydrous sodium sulphite dissolved in 20 c.c. of water, then 2 c.c. of concentrated hydrochloric acid, and diluting the mixture to 200 c.c. After one hour the reagent is ready for use. W. P. S.

New Reaction of Aldehydes. R. De Fazi. (*Gazz. Chim. Ital.*, 1921, **51**, I., 328-338.)—It has been already shown (*ANALYST*, 1916, **41**, 250) that when traces of acenaphthene and of a cyclic aldehyde are dissolved in absolute alcohol, and concentrated sulphuric acid is added to the solution so as to leave the two liquids separate, the surface of contact exhibits a coloured ring, often emerald green at first, but changing, sooner or later, to reddish-violet. The same colour reactions are given if the acenaphthene be replaced by fluorene, but the reaction is not due to the formation of condensation products. T. H. P.

Estimation of Salicylates and Phenol. W. P. Emery. (*J. Ind. Eng. Chem.*, 1921, **13**, 538-539.)—In a method proposed for the estimation of these compounds advantage is taken of the characteristic behaviour of the constituents, phenol and salicylic acid, towards iodine; the final product of the reaction in the presence of alkali or alkali carbonate is a purplish-red amorphous compound, $C_6H_2I_2O$, termed diiodophenylene oxide or tetraiodophenylene quinone. The reaction is represented by the equations:



Each mol. of phenol, salicylic acid, or acetylsalicylic acid yields one mol. of the iodine compound, whilst one mol. of salol yields two mols. of the same compound. The physical properties of the compound are such as to warrant its application to analysis. In the case of salol, about 0.1 gm. of the sample is weighed on to a small dry filter, and washed with successive quantities of chloroform until all soluble substances have been dissolved; the chloroform solution is evaporated at the ordinary temperature in a conical flask, the dry residue obtained is treated with 10 c.c. of 1 per cent. sodium hydroxide solution, and the mixture heated under a reflux apparatus, so that boiling begins in about two minutes. Successive quantities of 10, 30, and 50 c.c. of water are then added, the heating being so regulated that the mixture begins to boil in about three, five, and ten minute intervals respectively. Just before the last addition of water, 1 gm. of dry sodium carbonate is introduced into the top of the condenser, and washed down with the water. To the clear

boiling solution are now added 60 c.c. (or an excess) of $\frac{N}{5}$ iodine solution, the mixture again boiled, the condenser then rinsed with a small quantity of water, and the flask disconnected. A further 1 gram. of sodium carbonate is added, and the mixture boiled gently for twenty minutes; care must be taken during this period, as the evolution of carbon dioxide causes much frothing. The precipitate is then collected on a weighed filter, washed with not less than 200 c.c. of hot water, dried at 100° C., and weighed. The weight found is multiplied by 0.3113 to obtain the amount of salol present. Acetanilide, phenacetin, and caffeine do not interfere with the estimation, but when phenacetin is known to be present, the quantity of iodine solution mentioned above should be increased by 5 c.c. for each 0.1 gram. of phenacetin. With a mixture of salol and acetanilide, the filtrate from the precipitate is practically colourless; but when phenacetin is present the filtrate is coloured light yellow, so that it is not easy to recognise whether or not an excess of iodine is present.

W. P. S.

Quantitative Test of the Stability towards Heat of Nitroglycerin Explosives. M. Taliani. (*Gazz. Chim. Ital.*, 1921, 51, I., 184-193.)—A glass tube to contain the explosive is fitted with a ground cap, which is furnished with a tap, and is surmounted by a siphon tube half-filled with paraffin wax, and connected with a mercury manometer. The apparatus, with the exception of the manometer, is contained in a double copper vessel, which is closed by a double glass door, and in the jacket of which is a calcium chloride solution, with the boiling-point 120° C. for nitrated glycerine explosives, or 135° C. for nitrocellulose. The sample of the explosive is disintegrated so as to pass through a sieve of 0.6 mm. mesh, but not through one of 0.4 mm. mesh; and 1.3 grms. is introduced into the glass tube, and the apparatus is fitted together and placed in position in the bath, which has been previously heated to 120° (or 135°) C.; the tap at the cap of the tube and also one at the top of the closed tube of the manometer are left open for thirty minutes, and are then shut. The pressure necessary to maintain constant the volume of the contents of the tube holding the explosive is measured at five-minute intervals, the results being plotted against times as abscissæ. Each type of explosive corresponds with a characteristic decomposition curve.

T. H. P.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Manganese in Commonly Grown Legumes. J. S. Jones and D. E. Bullis. (*J. Ind. Eng. Chem.*, 1921, 13, 524-525.)—The following quantities of manganese were found in various leguminous plants, etc., the results being expressed as milligrams of manganese per kilo of air-dried substance: Vetch, 17 to 53; red clover, 19 to 70; Alsike clover, 40 to 140; alfalfa, 16 to 29; field peas, 20 to 52; sweet clover, 15 to 50; white clover, 33 to 35. The relative amounts in different parts of the plants were also estimated; the results obtained were as follows, and support the theory that the primary function of the manganese is catalytic (to the oxidising enzymes), since by far the largest amounts are present in the leaves:

| | Stems. | Flowers. | Leaves. | Seeds. | Pods. |
|-------------------|--------|----------|---------|--------|-------|
| Red clover | 20 | 66 | 84 | 12 | — |
| Alfalfa | 13 | 42 | 76 | 11 | — |
| Vetch | 11 | 17 | 33 | 10 | 6 |
| Field pea | 14 | 21 | 38 | 11 | 21 |

W. P. S.

Detection of Dextrose in Plants. M. Bridel and R. Arnold. (*Comptes rend.*, 1921, **172**, 1434-1436.)—The biochemical method of Bourquelot and Bridel (*ANALYST*, 1920, **45**, 175) has been adapted to the detection of dextrose in plants in general. The material under examination is extracted with boiling alcohol, the alcoholic extract dissolved in water, and the solution made up to definite volume, treated with lead acetate, and filtered. The filtrate is freed from lead by means of hydrogen sulphide, and evaporated to dryness under reduced pressure at a temperature not exceeding 50° C., and the residue extracted with hydrated ethyl acetate, and subsequently several times with boiling 95 per cent. alcohol. The united alcoholic extracts containing the sugars are distilled to dryness under reduced pressure in the presence of calcium carbonate, the residue dissolved in 50 per cent. methyl alcohol, the solution filtered, and the filtrate treated with emulsin in the proportion of 0.5 gm. per 100 c.c. The mixture is kept at about 20° C., and shaken at least once a day, and the reducing sugars estimated every ten days until their quantity ceases to diminish.

Estimation of Urea, Ammonia, and Amino-Acids in Urine after Precipitation of the Ammonia. M. J. Philibert. (*J. Pharm. Chim.*, 1921, **24**, 5-12, 49-58.)—After criticising the other methods for estimating the ammonia in urine, a modification of the method of Bournigault and Bith (*Comptes. rend. Soc. Biol.*, 1914, **1**, 114) is adopted which admits of the rapid estimation of ammonia, urea, and amino-acids, in the sample. The ammonia is precipitated as magnesium ammonium phosphate by adding to 40 c.c. of the urine 11 c.c. of a solution containing 100 grms. of monocalcium phosphate, and 10 c.c. of phosphoric acid per litre, 2 drops of phenolphthalein, and then 3 or 4 grms. of magnesia (free from carbonate), until, after mixing, the liquid is of a faint pink colour (excess of alkali must be avoided). The liquid is filtered with the aid of suction, the filtrate is kept apart, and the precipitate washed rapidly with 50 c.c. of water. The ammonia in the precipitate is determined by direct titration or by distillation under prescribed conditions; a correction of 25 mgrms. or 0.3 c.c. $\frac{N}{10}$ solution is allowed for the solubility of the magnesium ammonium phosphate. For the estimation of the urea 2 c.c. of lead sub-acetate solution are added to 12.5 c.c. of the filtrate from the above determination, the liquid is made up to 50 c.c., filtered, and 10 c.c. (= 2 c.c. of the urine) treated by the hypobromite process (*cf. ANALYST*, 1919, **44**, 240). The filtrate from the ammonia precipitation is also used for the estimation of the amino-nitrogen by a modification

of the formaldehyde process. A standard colour is prepared by adding to 25 c.c. of water (coloured to match urine by the addition of a few drops of tropæolin 0 or 00), 2 drops of phenolphthalein, then $\frac{N}{10}$ sodium hydroxide until a faint pink tint is obtained, after which 10 c.c. of neutralised formaldehyde solution 1 : 2 are added, and finally 0.3 c.c. of $\frac{N}{10}$ alkali. For the estimation 25 c.c. of the filtrate (= 20 c.c. of the urine) are acidified with dilute sulphuric acid, phenolphthalein added, and the liquid brought to the faint pink colour, treated with 10 c.c. of the formalin solution, and titrated with $\frac{N}{10}$ sodium hydroxide until the red colour equal to that of the standard is obtained. From the number of c.c. of standard alkali required the amino-nitrogen is calculated, after deduction of 0.3 c.c. for the solubility of the magnesium ammonium phosphate, and 0.3 c.c. for the excess of alkali required to produce the standard red colour. Details as to the colour changes of the indicators and possible sources of error are discussed at length.

H. E. C.

WATER ANALYSIS.

Colorimetric Method for the Estimation of Hydrogen-Ion Concentration in Water. I. M. Kolthoff. (*Pharm. Weekblad*, 1921, 58, 1005-1020.)—For the estimation of its hydrogen-ion concentration the water is treated with neutral red solution, and the tint is compared with standardised acid and alkaline solutions of the same indicator contained in two wedge-shaped tubes attached to each other by Canada balsam. By means of a movable graduated scale the value of P_H for the corresponding tint can be read directly. In water analysis, a knowledge of the hydrogen-ion concentration is chiefly of importance in determining the carbon dioxide content when the bicarbonate content has been found.

$$[\text{CO}_2] = [\text{H}^+] [\text{HCO}_3^-] / 3 \times 10^{-7}.$$

The use of the hydrogen electrode for estimating the hydrogen-ion concentration in water is not recommended.

W. J. W.

AGRICULTURAL ANALYSIS.

Methods of Estimating the Amount of Colloidal Material in Soils. C. J. Moore, W. H. Fry, and H. E. Middleton. (*J. Ind. Eng. Chem.*, 1921, 13, 527-530.)—Large quantities of soil colloids were obtained by shaking 25-lb. portions of the soil with 125 lb. of water, separating the liquid, and passing it through a Sharples centrifugal machine; the opalescent liquid issuing from the machine was then filtered through batteries of Pasteur-Chamberlain filter-tubes, and the slimy, sticky mass collecting on the tubes was removed, stirred with water, and collected on clean filter-tubes. This material, to which the name "ultra-clay" has been given, consists mainly of hydrated aluminium silicate, and has every appearance of being a true colloid. It absorbs ammonia or dyestuffs readily, but loses this property after being heated at 1130° C.; the absorption is the same whether the material is in the form of compressed pellets or loose, incoherent powder. To estimate the colloidal matter the "ultra-clay" was dried at 110° C. for twenty-four hours, then placed in a U-tube immersed in boiling water, and the air exhausted from the tube. The U-tube was

now cooled in an ice-bath and dry ammonia gas passed through it. The absorbed ammonia was subsequently estimated by heating the tube and collecting the expelled ammonia in boric acid solution, and titrating the latter with $\frac{N}{10}$ sulphuric acid, methyl orange being used as indicator. From 93 to 110 c.c. of ammonia were absorbed per c.c. of two specimens of "ultra-clay" examined (the volume of the latter was calculated from the specific gravity). A sample of soil from which the "ultra-clay" was obtained (the specimen absorbing 110 c.c. of NH_3) absorbed 27.7 c.c. of ammonia per c.c. of soil under the same conditions, and 1.4 c.c. after it had been heated at 1130°C . Deducting the 1.4 c.c. of ammonia absorbed by non-colloidal material from 27.7 c.c., left 26.3 c.c. absorbed by the soil colloids; therefore the colloidal content of the soil was 28.9 per cent. Another method of estimating the colloidal content of the soil was based on the absorption of malachite green from a solution containing an excess of sodium oxalate; this method yielded results identical with those obtained by the ammonia absorption method.

W. P. S.

Estimation of Dicyanodiamide and of Urea in Fertilisers. E. Johnson.

(*J. Ind. Eng. Chem.*, 1921, **13**, 533-535.)—A volumetric method described for the estimation of dicyanodiamide depends on the formation of the complex, silver picrate dicyanoguanidine. For material containing from 5 to 15 per cent. of dicyanodiamide nitrogen, a 5-grm. portion is shaken for three hours with 450 c.c. of water and 5 c.c. of glacial acetic acid, and the mixture is then diluted to 500 c.c. and filtered. To 100 c.c. of the filtrate are added 5 c.c. of 20 per cent. nitric acid and 20 c.c. of sodium picrate solution, the mixture is cooled to 5°C ., and silver nitrate solution (7.584 grms. per litre) is added, drop by drop, until a slight excess (about 2 c.c.) over what is required for the dicyanodiamide, assumed to be present, has been introduced. After fifteen minutes the mixture is diluted to 200 c.c. and filtered, 5 c.c. of nitric acid and 3 c.c. of 5 per cent. ferric sulphate solution are added, and the excess of silver is titrated with thiocyanate solution. If 5 grms. of sample were taken, each c.c. of the silver nitrate solution used for the precipitation is equivalent to 1 per cent. of dicyanodiamide nitrogen. The sodium picrate solution is prepared by neutralising 7.5 grms. of picric acid with sodium carbonate and diluting the solution to 100 c.c.; it must be used at about 40°C . to avoid crystallisation of the sodium picrate. A method for the estimation of urea is based on the fact that this compound forms, with oxalic acid, a salt soluble with difficulty. Five grms. of the fertiliser are dried and shaken with 100 c.c. of amyl alcohol, the mixture is filtered, 50 c.c. of the filtrate are mixed with an equal volume of ether, and the urea is precipitated by the addition of 25 c.c. of a 10 per cent. solution of anhydrous oxalic acid in amyl alcohol. After thirty minutes the precipitate of urea oxalate is collected on a filter, washed twice with a mixture of equal volumes of amyl alcohol and ether, then once with ether, dried under reduced pressure, and weighed. The precipitate contains 57.01 per cent. of urea.

W. P. S.

INORGANIC ANALYSIS.

Estimation of Hydrogen-Ion Concentration in Small Volumes of Liquid by Means of Indicator Papers. J. M. Kolthoff. (*Pharm. Weekblad*, 1921, 58, 961-970.)—It has been shown that indicator papers are not reliable with very dilute solutions of acids and bases (Kolthoff, *Pharm. Weekblad*, 1919, 56, 175); on the other hand, in presence of a buffer mixture, the results agree with those obtained with indicator solutions, provided certain conditions are observed. The indicator paper should be prepared from hardened filter-paper. The drop should be applied by means of a marked capillary tube to insure uniformity of volume in each case, and the colour should be noted after a given interval and before the drop has dried. From investigation of a number of indicator papers, details of the preparation and use of which are given, the following values of P_{H} , for the estimation of which the various indicators are suitable, are given: Congo red, 2.5-4.0; methyl orange, 2.6-4.0; blue lacmoid, 4.8-6.0; alizarin, 4.6-5.8; metachrome red, 6.0-8.5; brilliant yellow, 6.8-8.0; red litmus, 6.6-8.0; blue litmus, 6.0-7.8; azolitmin, 6.0-8.0; α -naphtholphthalein, 8.2-9.5; and turmeric, 7.5-9.5. Methyl red, phenolsulphophthalein, rosolic acid, and neutral red were found to be unsuitable. Hæmatoxylin paper may be used with strong acids; it gives a salmon colour with $\frac{N}{2}$ —, and a rose colour with 3 to 4 *N* hydrochloric acid. W. J. W.

New Reagent for Ammonia. C. D. Zenghelis. (*Comptes rend.*, 1921 173, 153-155.)—This reagent, which consists of 20 per cent. silver nitrate solution mixed with three volumes of commercial formaldehyde (33 or 37 per cent.), should be prepared shortly before being used. The solution to be tested is rendered strongly alkaline by addition of sodium hydroxide or carbonate, and 0.5 to 1 c.c. thereof placed in a test-tube about 12 cm. in height, covered by a watch-glass, from which hangs a drop of the reagent; a little water is placed in the watch-glass to serve as a condenser, the tube being then heated on a sand-bath until condensed drops collect round the reagent. With as little as 1 c.c. of 0.0002 *N*-ammonia, containing 0.00034 mgrm. of ammonia, a distinct annular silver mirror forms in the course of a few seconds. The same quantity of ammonia dissolved in a large quantity of water is detectable after the liquid has been first evaporated with a drop of dilute sulphuric acid to a volume of 0.5 to 1 c.c. The reagent will reveal the presence of ammonia in drinking water with which Nessler's reagent fails or gives doubtful results.

T. H. P.

Estimation of Silver and its Separation from Lead and other Metals by Means of Hypophosphorous Acid. L. Möser and T. Kittl. (*Zeitsch. anal. Chem.*, 1921, 60, 145-161.)—When a hot dilute solution of a silver salt is treated with an excess of hypophosphorous acid (100 per cent. more than is required by theory), the silver is precipitated completely; further heating causes the finely divided silver to coagulate so that it may be collected on a filter, washed with hot water, ignited, and weighed. Contrary to the statement by Mawrow and Mollow (*ANALYST*, 1909, 34, 115), the authors find that washing with hot water does not

cause the precipitate to pass through the filter. The method may be applied to the separation of silver from lead, cadmium, zinc, etc., since the hypophosphites of these metals are soluble in hot water.

W. P. S.

Volumetric Estimation of Mercury. E. Biilmann and K. Thaulow. (*Bull. Soc. Chim.*, 1921, **29**, 587-592.)—I. Allyl alcohol reacts with mercuric compounds to form a complex organo-mercuric compound: $C_3H_5.OH + HgX_2 = (C_3H_5O)HgX + HX$. On treatment with sodium hydroxide this compound is converted into a hydroxide which is so feebly basic that phenolphthalein is not turned red until all the complex salt is converted thus: $(C_3H_5O)HgX + NaOH = (C_3H_5O)HgOH + NaX$. On treating the hydroxide with potassium bromide, quantitative liberation of potassium hydroxide occurs— $(C_3H_5O)HgOH + KBr = (C_3H_5O)HgBr + KOH$. Consequently, titration of the liquid with standard acid enables the mercury present to be estimated. From 2 to 3 c.c. of allyl alcohol are added to the mercury salt dissolved in nitric or sulphuric acid (about 5-N); the solution is then made alkaline to phenolphthalein with sodium hydroxide (2-N), and neutralised with sulphuric acid (0.2-N). A solution containing 5 grms. of neutral potassium bromide is then added, and the potassium hydroxide liberated is titrated in the usual way with standard acid.

II. An iodimetric method is based on the reaction— $HgO + KI + H_2O = HgI_2 + 2KOH$. For the estimation of mercury in salts such as the nitrate or sulphate, the salt is dissolved in an excess of the dilute acid present as radicle in the salt, the liquid is rendered alkaline to phenolphthalein with sodium hydroxide, and neutralised with very dilute sulphuric acid (the colour change is not masked by the precipitated yellow mercuric oxide); potassium iodide is then added, and the liquid thoroughly mixed in a corked flask, and finally the potassium hydroxide liberated is titrated with standard acid. The results obtained with known amounts of mercury agreed closely with those obtained by the first process and with the theoretical values.

R. G. P.

Estimation of Small Amounts of Lead in Brass. F. W. Glaze. (*J. Ind. Eng. Chem.*, 1921, **13**, 553-554.)—A method suitable for the estimation of quantities of lead of less than 0.06 per cent. in brass consists in dissolving 8.643 grms. of the sample in 30 c.c. of dilute (1 : 1) nitric acid, complete solution being effected by adding 15 c.c. of concentrated nitric acid and warming the mixture. The solution is then evaporated until cupric nitrate crystallises out, cooled, 5 c.c. of nitric acid and a small quantity of water are added, and the mixture is heated until all crystals have dissolved, and then diluted to 100 c.c. and electrolysed. Cylindrical gauze electrodes and a current of N.D.₁₀₀ of 1.5 ampères and 3 volts are employed. After about one hour the electrolyte is drawn off by means of a siphon, and the anode is washed with distilled water and alcohol, dried at 210° C. for thirty minutes, cooled, and weighed. The electrode is then cleaned, dried, and again weighed, the difference between the weights giving the weight of the lead dioxide; this weight multiplied by ten gives the percentage of lead in the brass.

W. P. S.

[This method has been used for many years in a well-known metallurgical laboratory.—EDITOR.]

Estimation of Nitrates in Bismuth Salts by means of Titanium Trichloride and Devarda's Alloy. T. McLachlan. (*Pharm. J.*, 1921, 106, 477-478.)

—Reduction of the nitrate to ammonia by means of titanium trichloride as described by Knecht (*ANALYST*, 1915, 40, 172) is best carried out in approximately neutral solution, a small excess of alkali being added before the ammonia is distilled; if a large excess of alkali was present at the beginning, the results obtained are sometimes much too low. The following procedure is recommended when the reduction is made with Devarda's alloy (copper, 50, zinc, 5, aluminium, 45 parts): Five grms. of the bismuth salt are mixed with 150 c.c. of water, 5 c.c. of alcohol, and 50 c.c. of 33 per cent. potassium hydroxide solution, and 8 grms. of the alloy are added. After about ten minutes the mixture is steam-distilled and the ammonia collected in a known amount of standard acid and titrated in the usual way. The method may be applied to the determination of nitrate in any bismuth salt, and yields consistent and trustworthy results.

W. P. S.

Estimation of Zinc as Ammonium Zinc Phosphate. G. Luff. (*Chem. Zeit.*, 1921, 45, 613-614.)—The precipitate of ammonium zinc phosphate is slightly soluble in water and more so in presence of ammonium chloride; in the latter case the solubility is to a great extent reduced by employing excess of diammonium phosphate as precipitating reagent.

W. J. W.

Gas Volumetric Method of Estimating Aluminium. L. Losana. (*Giorn. Chim. Ind. Appl.*, 1921, 3, 239-241.)—A 150 to 200 c.c. flask is charged with 0.2 gm. of the aluminium or aluminium alloy in fine turnings and 30 c.c. of boiled water, and closed by a two-holed stopper carrying a tapped funnel and a gas delivery tube which has a short rubber tube inserted in it and turns up at the lower end. The tube of the funnel is completely filled with water, and 15 c.c. of 20 per cent. potassium hydroxide solution placed in the funnel. The water in the flask is boiled to expel all air from the flask, the end of the delivery tube being then placed under a graduated tube filled with water and inverted in a trough of water and the flame removed; as soon as the pressure in the flask falls a little, the delivery tube is stopped by clipping its rubber insertion, the potash solution introduced into the flask, the flame immediately restored, and the clip removed when a slight pressure develops. The hydrogen liberated collects in the graduated vessel, the liquid being kept boiling for five minutes after evolution of gas ceases. The volume of the gas is read and reduced to 0° and 760 mm. pressure; 1 c.c. of hydrogen corresponds with 0.00802 gm. of aluminium. An alloy which may possibly be attacked by the boiling water is placed in a test-tube filled with water, and this suspended on a wire frame below the stopper of the flask, so that it can be made to fall into the boiling alkali solution. Any magnesium present acts similarly to the aluminium, and must be separately estimated and its amount deducted from the apparent quantity of aluminium, but the method is not invalidated by zinc, iron, or the small proportions of silicon and sodium normally present, and is especially suitable for alloys containing variable amounts of an inert element, such as copper, with approximately constant amounts of the other constituents; use may then be made of an empirical factor, in place of the theoretical

one, to obtain the percentage of aluminium. For alloys containing between 100 and 70 per cent. of aluminium the method gives good results. The measuring vessel consists suitably of a bulb of a known capacity of about 200 c.c., with a lower tube graduated from 200 to 300 c.c.

T. H. P.

Estimation of Cobalt and Nickel in Cobalt Steels. G. E. F. Lundell and J. I. Hoffman. (*J. Ind. Eng. Chem.*, 1921, **13**, 540-543.)—From 2 to 4 grms. of the sample are dissolved in hydrochloric acid, oxidised with nitric acid and silica and tungstic acid, separated by filtration, the filtrate treated with sodium hydroxide solution, and any insoluble matter collected, dissolved in hydrochloric acid, and added to the main solution. The latter is evaporated, but not to complete dryness; concentrated hydrochloric acid is added, and the greater part of the iron, together with the molybdenum, is separated by extraction with ether. The residual acid solution is then heated with sulphuric acid until fumes of the latter are evolved, and, after dilution, the chromium, vanadium, and manganese are oxidised by potassium persulphate. The hot oxidised solution is poured into hot sodium hydroxide solution, the precipitate is collected, dissolved in dilute sulphuric acid with the aid of sodium hydrogen sulphite, and the copper is removed by treatment with hydrogen sulphide. After the solution has been boiled and re-oxidised, a double precipitation with ammonia serves to remove iron. The combined filtrates from the ferric hydroxide precipitates are evaporated to a volume of 100 c.c., neutralised with ammonia, and an excess of 35 c.c. of ammonia (sp. gr. 0.9) and 2 grms. of sodium hydrogen sulphite are added. The solution is diluted to 150 c.c. and electrolysed for eight hours, gauze electrodes and a current density of 0.2 to 0.3 ampère per sq. dm. being used; the cathode is then washed with cold water, dried at 100° C., and weighed. Traces of nickel and cobalt remaining in the electrolyte are recovered by boiling with an excess of ammonium persulphate, keeping the solution strongly ammoniacal in order to precipitate the manganese, filtering the mixture, and treating the filtrate with hydrogen sulphide. The precipitated sulphides are collected, washed, ignited, and weighed; the weight (usually not more than 1 mgrm.) is multiplied by the empirical factor, 0.75, and the result added to the weight of metals found on the cathode. The nickel and cobalt deposited on the cathode, and the small quantity of oxides recovered as described, are dissolved in 20 c.c. of nitric acid (sp. gr. 1.42), the solution is neutralised with ammonia, then rendered just acid with hydrochloric acid, and the nickel precipitated with dimethylglyoxime; the mixture is rendered slightly ammoniacal, and after two hours the precipitate is collected, dissolved in 20 c.c. of warm nitric acid, and re-precipitated as before. The precipitate is finally collected, washed, dried at 120° C., and weighed. The quantity of nickel present is calculated from the weight of the precipitate, and the amount of cobalt is obtained by difference. Methods are also described for the estimation of chromium, vanadium, copper, and manganese, in the same portion of steel.

W. P. S.

Estimation of Calcium and Magnesium in various Salt Mixtures. E. Canals. (*Bull. Soc. Chim.*, 1921, **29**, 583-585.)—Iron and aluminium phosphates adsorb considerable quantities of calcium and magnesium salts when the latter are

present in relatively large proportions, but by adding acetic acid, drop by drop, with vigorous stirring, for several minutes and washing the iron and aluminium phosphates with boiling water containing acetic acid, all the calcium and magnesium passes into solution. (Cf. ANALYST, 1921, 46, 216.) R. G. P.

Constitution of Sodium Perborate. F. Foerster. (*Zeitsch. angew. Chem.*, 1921, 34, 354-355.)—The composition of sodium perborate is represented by the formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ and not by $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$. When the salt after dehydration at 50° to 55° C. is heated *in vacuo* to 120° C., it loses appreciable amounts of water, and the residue consists chiefly of $(\text{NaBO}_2)_2\text{O}_2$ with some $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ and metaborate. The compounds $(\text{NaBO}_2)_2\text{O}_2$ differ in properties from NaBO_3 ; the existence of a substitution product of hydrogen peroxide, having the composition

$\text{NaOB} \begin{array}{l} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, and analogous to persulphates and percarbonates, is implied.

W. J. W.

Use of "Fornitral" for the Detection and Estimation of Nitric Acid. (*Ann. Chim. Anal.*, 1921, 3, 207-208.)—"Fornitral" (prepared by Poulenc Frères) contains two mols. of formic acid attached to one mol. of endo-anilodiphenyldihydrotriazol ($\text{HCOOH})_2(\text{C}_6\text{H}_6)_3(\text{N}_4\text{C}_2\text{H})$. It is intended for use instead of nitron and is superior to the latter, as its aqueous solution is stable, whilst nitron must be used in acetic acid solution and deteriorates on keeping. The addition of 5 to 6 drops of "fornitral" in the cold to 1 c.c. of water containing 0.03 mgrm. of nitric acid gives a precipitate immediately; with 0.015 mgrm. of nitric acid a precipitate is obtained after two hours; and with 0.0075 mgrm. of nitric acid, after five hours. Precipitation is facilitated by rubbing the tube with a glass rod. The reagent is particularly suited for the estimation of nitric acid in presence of organic matter (*e.g.*, soil and plant extracts, culture media, fertilisers, effluents). The process is not affected by tartaric or citric acid, sucrose or glucose, urea, asparagin, aspartic acid, alkali phosphates, or salts of magnesium, calcium, lead or aluminium, but oxalic acid, when present in considerable quantities, causes high results. Nitrated compounds containing nitro groups capable of conversion to nitric acid by oxidation or hydrolysis can be estimated. For the estimation of nitric acid, the solution containing about 0.1 grm. of nitric acid per 100 c.c. is acidified with 10 drops of dilute sulphuric acid, heated nearly to boiling, and treated with 10 c.c. of the reagent (10 per cent.). The liquid is then cooled, placed in ice for about two hours, and filtered with the aid of suction through a Neubauer, Gooch, or (preferably) alundum crucible, and the precipitate is washed with a small quantity (12 c.c. in three washings) of cold water, dried at 100° to 110° C. for about an hour, and weighed. The weight multiplied by 0.168 gives the amount of nitric acid. R. G. P.

PHYSICAL METHODS, APPARATUS, ETC.

Determination of Refractive Indices of Oils. H. S. Simms. (*J. Ind. Eng. Chem.*, 1921, 13, 546-547.)—The oil to be tested is drawn into a thin-walled bulb tube, and the lower end of the tube is then sealed; the bulb should have

a diameter of 0.5 inch, and be filled completely with the oil. The filled bulb is then immersed in another oil of known refractive index, and contained in a wide test-tube. The bulb is now moved up and down, while the observer looks through it at a distant object. If the image rises as the bulb is raised, and sinks as the bulb is lowered, the refractive index of the oil is *less* than that of the medium (the oil in the test-tube), the bulb acting as a concave lens in air. If the bulb is filled with an oil having a greater refractive index than that of the medium, the image sinks when the bulb is raised, and rises when the bulb is lowered. By having a series of test-tubes containing oils of known, but different, refractive indices, and testing the filled bulb in each of these, the refractive index of the sample may be found within 0.0005 of the true value.

W. P. S.

Gold Cathodes for Electrolytic Work. A. B. Andrews. (*J. Ind. Eng. Chem.*, 1921, **13**, 560.)—Open cylinder cathodes made of 24-carat gold were found to be quite as satisfactory as platinum cathodes for the electrolytic deposition of copper; the anode must still be made of platinum.

W. P. S.

New Apparatus for Steam Distillation. E. A. Roff. (*Pharm. J.*, 1921, **107**, 28-29.)—The flask containing the substance to be distilled is placed entirely in the steam-generating vessel, which consists simply of a tin fitted with a lever-lid; two holes are provided in the lid, and these are closed by rubber stoppers. A long tube passes through one of these stoppers and extends into the water in the tin, thus acting as a safety tube, and the delivery tube from the flask passes through the other stopper. When the water in the tin is boiled, steam enters the flask through a tube, the upper end of which reaches just above the cork closing the flask, whilst its lower end extends into the liquid or other substance in the flask.

W. P. S.

Fractional Distillation with Contact-Ring Stillheads. R. Lessing. (*J. Soc. Chem. Ind.*, 1921, **40**, 115-119t.)—For laboratory stillheads contact-rings are employed in which a diametrical partition extends the whole or part of the way across without being joined to the ring so as to interfere with the flow of liquid. Apart from their simplicity, these rings have advantages over other stillheads in that they present a large surface per unit of volume, and create turbulence in the currents of vapour and condensate by which "channelling" is avoided. Comparative curves are given for the distillation of a 1:1 mixture of benzene and toluene with various types of stillhead and with a plain stillhead of 4 cm. diam. and 140 cm. height, filled with $\frac{1}{4}$ -inch aluminium contact-rings. In the latter case almost complete separation was effected; benzene and toluene distilled over to the extent of 47 and 48 per cent. respectively, each within 1°, and only 5 per cent. of the mixture remained in the middle fraction. A very sharp curve was obtained in the fractionation of crude benzol from coke-oven gas, using a ring-filled stillhead and a short reflux condenser. The influence of the stillhead dimensions, heat insulation, and reflux condensing is indicated in four cases. In the fractional distillation of commercial fusel oil, using a stillhead of 4 cm. diam. and 140 cm. height, filled with $\frac{1}{4}$ -inch copper rings, and lagged with asbestos to within 10 cm. of

the top, the following fractions were obtained: From 78.0° to 87.4° C., 9.5 per cent. by volume, consisting of a mixture of aqueous ethyl and *n*-propyl alcohol; from 87.4° to 88.6° C., 19.5 per cent.; and from 88.6° to 89.0° C., 24.6 per cent., these fractions consisting of propyl alcohol. Water distilled over first at 89.1° C., and sharply indicated the beginning of isobutyl alcohol; the fraction between 89.0° and 89.5° C. was collected in two layers. When the last drop of water had distilled over, the curve showed a perfect right angle. The remainder of the isobutyl alcohol came over in an anhydrous condition between 89.5° and 107.2° C., after which amyl alcohol was collected in the remaining fractions. When aluminium rings were used for the distillation of the same sample, abnormal results were obtained. After the temperature had become constant at 89.1° C. it suddenly dropped, and at 79.6° C. white fumes were evolved; a sudden rise of temperature then occurred, followed by a drop and rise at 97.2° C., and again at 103.0° C. Aluminium hydroxide was found in the flask. The phenomenon is explained by the formation of aluminium butoxide to such an extent that the vapours reaching the thermometer were insufficient to keep it heated; air then diffused back, and traces of water in the mixture of water and butyl alcohol stopped the reaction. An interesting feature was the fact that, when the action occurred, the column still contained 69 per cent. of a mixture of butyl alcohol and water of constant boiling-point, partly as vapour and partly as condensate. The division between the moist and anhydrous portions of the column was an extremely sharp one, and the rings acted as a perfect seal against moisture.

W. J. W.



THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

PASS LIST.

EXAMINATIONS: JULY, 1921.

THE following candidates have been successful in the recent examinations, and have been duly elected Associates of the Institute:

Examination in General Chemistry: Campbell, Alan Newton, B.Sc. (Lond.); Doolan, James Joseph; Evans, Benjamin Beardmore, B.Sc. (Birm.); Hand, Percy George Terry; Jenkin, John Watson; Pugh, William; Ridge, Bert Pusey; Woolf, Sidney Samuel, B.Sc. (Lond.).

Examination in Metallurgical Chemistry: Storer, George Paterson.

Examination in Organic Chemistry: Kenyon, Frank; Sheldon, Francis Joseph, A.R.C.S., B.Sc. (Lond.).

Examination in the Chemistry of Foods and Drugs, etc.: Martin, Charles William; Mooney, Paul Michael, B.Sc. (Lond.); Woodward, Miss Elsie.

Examination in Chemical Technology (Soap, etc.): Smith, David Dow. (*Coke Oven Practice, etc.*): Whitaker, John Wilfrid, B.Sc. (Lond.).



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FOOD CONTROL.

STATUTORY RULES AND ORDERS.

No. 1056, 1921.

ORDER DATED JUNE 24, 1921, MADE BY THE BOARD OF TRADE UNDER THE MINISTRY OF FOOD (CONTINUANCE) ACT, 1920 (10 AND 11 GEO. 5, C. 47), AND THE MINISTRY OF FOOD (CESSATION) ORDER, 1921, AMENDING THE MILK (ENGLAND AND WALES) ORDER, 1921, AND THE MILK (SCOTLAND) ORDER, 1921.*

1. The following clause shall be substituted for Clause 5 of the Milk (England and Wales) Order, 1921, and Clause 6 of the Milk (Scotland) Order, 1921 :

“ For the purposes of this Order the expression ‘ milk ’ shall include skimmed, separated, and butter milk, and any milk which has been submitted to any one or more of the following processes—viz., sterilisation, pasteurisation, homogenisation, or any other like process, but shall not include condensed milk.”

2. Copies of the above-mentioned Orders hereafter to be printed under the authority of His Majesty's Stationery Office shall be printed with the amendment provided for by this Order, and the Orders shall, on and after June 30, 1921, be read and take effect as hereby amended.

* * * * *

REVIEWS.

THE FORMATION OF COLLOIDS. By THE SVEDBERG (Professor of Physical Chemistry in the University of Upsala). Pp. vi+127. London: J. and A. Churchill. 1921. Price 7s. 6d. net.

This monograph is the first of a series by Dr. Svedberg on the Physics and Chemistry of Colloids. According to the author: “ In the first monograph, I mean to give a survey of the processes which cause the formation of colloids—or of heterogeneous systems with a relatively large boundary surface on the whole (disperse systems according to W. Ostwald)—especially with regard to the conditions that determine the degree of subdivision of the systems formed. As the formation of gels is a change of state within the disperse system, it will not be considered in this monograph, which deals with the formation of colloids from non-colloid material.”

* Cf. ANALYST, 1921, 305.

Dr. Svedberg is thoroughly at home in this little book, for his own laboratory has long been famous for the researches on the formation of colloids, especially by electrical methods; this work in particular is well described and well illustrated. An extensive field is covered in little compass, being admirably summarised, critically considered, and clearly stated. Over two hundred references to the literature are made.

The following quotation from the Introduction will serve to indicate the skeleton ideas upon which the discussion is built:

“Colloids or disperse systems in general may be formed in two ways, differing in principle: by condensation, or by dispersion. In one case matter is brought together within a smaller boundary surface than before; in the other case the matter is dispersed so that the specific surface is increased. In many cases diverse systems are formed by a combined process of condensation and dispersion. Often on superficial observation the process may be considered, for instance, as a dispersion, while an intimate analysis of the phenomenon shows that a condensation process is inserted so as to make such a process the direct cause of the formation of the disperse system. . . . If the state of the system in the period that directly precedes the formation of the disperse system be taken into consideration, the classification of the processes of formation in condensation and dispersion will evidently be clearly defined.”

After a discussion of the formation of disperse systems *in vacuo*, a very clear account is given of the various methods of electric pulverisation. Fifty-three pages are then devoted to the study of Condensation Processes in the formation of disperse systems in liquids and in solids. The author here gives a succinct account of the numerous investigations on the formation of the classical colloid, the gold sol, and of Odén's investigations on the relation between degree of dispersion and concentration (BaSO_4 sols). The final section, on dispersion processes, includes very brief treatments of (1) partial dissolution, (2) grinding, and (3) emulsification.

The subject of emulsification might well have received greater consideration, since, as Dr. Svedberg agrees, “the formation of disperse systems by emulsification is important both from a theoretical and from a practical point of view.” The reversal of phases, the recently described method of intermittent emulsification, and the question of the limiting concentration of a purely diphasic emulsion (as distinct from concentrated emulsions obtained by using a third reagent), are matters clearly to be included in any general discussion on the formation of disperse systems.

The book is well written, and published in an attractive form. Very few errors have been noticed—*e.g.*, thioic acid, for thiosulphuric acid (p. 90), and $\text{Na}_2\text{O}_3\text{S}_3$ for $\text{Na}_2\text{S}_2\text{O}_3$ (p. 86). Readers will consider it strange to find the symbol J in KJ, AgJ and NaJ (p. 101) for iodides.

All students of colloids will welcome this little book, and find it most useful.

WILLIAM CLAYTON.

COKE OVEN AND BY-PRODUCT WORKS CHEMISTRY. By THOMAS BIDDULPH-SMITH.
Pp. x + 180. London: Charles Griffin and Co., Ltd. Price 21s. net.

A work bearing this title, written by one actively engaged in the industry, might reasonably be expected to be a treatise on the chemistry of coke-oven practice and

the application thereto of modern chemical and physical methods of control and examination. The author has, instead, given us a manual of testing such as might have been written by a "works chemist" who was not allowed on the works proper, but was confined to the laboratory. The examination of coal and coke is dealt with in four pages, thirteen lines only being devoted to the rather important matter of sampling. Another twenty-four pages are devoted to the examination and analysis of gases.

In dealing with the liquid products of the carbonisation of coal the treatment is much more thorough, and the physico-chemical methods of determining benzene, toluene, xylene, etc., in commercial benzole and solvent naphtha due to Colman, Northall-Laurie, Spielmann, and their co-workers are given in full, seven folding plates of the necessary graphs enabling a worker to use these methods without frequent reference to several large volumes. This important feature alone will make the work extremely useful to those chemists whose work includes the examination of such complex mixtures as commercial hydrocarbons.

It is to be regretted that the author has not dealt with calorimetry, pyrometry, and the physics of his subject generally a little more thoroughly. He has treated them so briefly that little could be gathered as to the use of some of the instruments described or the means which should be taken to secure reasonable accuracy during continued use.

Some uncertainty is shown as to the spelling of "benzole." On p. 138, Appendix I., Dr. Spielmann's translation of Weger's monograph on "Some Constituents of Coal Tar and their Properties" correctly states that the use of the German termination *ol* for both commercial and pure benzene and toluene "is objectionable as being unnecessary and also in causing confusion, as it is properly reserved for the alcohol group (phenol, not phenole)." "Benzol," however, occurs throughout the book, but in the index "benzole" only is given. The misprint *ortha* cresol occurring three times on p. 43 somewhat offends the eye.

This book, notwithstanding the shortcomings indicated, is a valuable contribution to the literature of chemical industry, more especially as there are full references to the original sources of information. It is to be hoped that in a new edition, revised in a more leisurely manner, the author may give us a work more representative of his knowledge and experience.

In addition to Appendix I. already mentioned, a second appendix contains many useful numerical and other data.

J. H. COSTE.

CRITICAL MICROSCOPY. By A. C. COLES, M.D., D.Sc. Pp. viii + 100. London: J. and A. Churchill, 1921. Price 7s. 6d. net.

The title of this work gives one a mild feeling of surprise by the thought that the small capacity of the volume should be sufficient to contain the whole of the subject indicated. Further investigation, however, shows that the contents are limited to the application of critical microscopy in the study of bacteriology and protozoology only, and some indication of this might have been given in the title or sub-title.

The first thirty-three pages describe the microscope and its various accessories, whilst the remainder of the book is devoted to manipulation, photomicrography, and one-and-a-half pages to the staining and mounting of objects.

The general style of the book is decidedly fragmentary, owing to the frequent interposition of extracts from the works of eminent microscopists, including many from the writings of E. M. Nelson, expressed in his usual unpleasantly interrogative style. So large a proportion of the subject-matter of the book is derived from the latter writer, that he is entitled to have his name coupled with that of the author upon the title-page. The information furnished, based largely upon the author's experience, is excellent, and should be of great value to any worker who, having mastered the elementary principles of microscopy, desires to obtain the best results possible from his instrument. Careful and accurate descriptions are given of methods for determining magnifying powers, optical indices, cover-glass correction, etc., and the means necessary for securing correct critical illumination is dealt with in an admirable manner. Any worker applying the principles and methods of manipulation advocated in this volume should meet with little difficulty, even when using the highest magnifications.

It is perhaps too much to expect that a book of this type should be free from errors, but such as occur are fortunately not serious. On p. 12 we are informed that "the Zeiss and Winkel lenses are . . . engraved 10 and 12, which . . . refer to the thickness of the cover-glass in millimetres," whilst on p. 72, line 9, "uncovered objective" should obviously read as "uncovered object." On p. 93, E. M. Nelson makes light of the effects of vibration during exposure in photomicrography, but the reviewer has lost many plates in the past from this cause, even when using a magnification of $\times 500$, when working in a laboratory adjoining an electrical power-house, and on other occasions in a building the foundations of which were close to the District Railway. The method advocated on p. 96 for the removal of dried balsam, cement, etc., from slides by the use of a knife is hardly one to be recommended, since the surface is liable to be scratched, and such blemishes must be very confusing when examining dry unmounted films microscopically. Information of but little value is given in reference to a micrometer for measuring the thickness of cover-glasses, etc., on p. 31, where the price is given as "pre-war 3s. 9d." The cost of this appliance at the present time is likely to be of more use. We are informed in the Preface that the author has "also given a short account of photomicrography with a very simple camera, by means of which one is able to take . . . sixteen photographs on a quarter-plate," but on referring to p. 89 for the method employed we find that "it is very difficult to describe on paper," and the only information obtainable is that a piece of sheet zinc with a hole 25 by 19 mm. cut in it is used.

The Index provided shows evidence of hurried compilation, for, whilst containing some incomplete references, such as "Back of objective," "Dust and dirt," "Indian ink method," and "Measurement," other subjects contained in the volume, including "Slides, cleaning of," "Development of plates," "Vibration in photomicrography," "Staining of objects," etc., are omitted.

The illustrations throughout the volume are good, and the twenty-seven photomicrographs of pathogenic protozoa, with magnifications ranging from $\times 400$ to

× 3,000, are excellent examples of the author's results, although seen at a disadvantage against the white background surrounding them. T. J. WARD.

A FRENCH-ENGLISH DICTIONARY FOR CHEMISTS. By A. M. PATTERSON, PH.D. Pp. 384. New York: J. Wiley and Sons, Inc. London: Chapman and Hall. Price 18s. net.

Some twenty years ago a German chemical society planned the publication of a complete chemical dictionary in English, French, and German, in which place was to be found for all the technical terms associated with each branch of chemical industry. Unfortunately, after an immense amount of material had been compiled, the scheme had to be abandoned for lack of funds, and the chance of an ideal chemical dictionary in the three languages was lost.

Apart from such an elaborate work as this, which could only have been produced by the collaboration of a large number of chemists, there has long been a demand for smaller dictionaries in French and German, containing most of the words which chemists need to know in order to read chemical and general scientific papers in those languages. To meet this want a concise German chemical dictionary was compiled, four years ago, by Dr. Patterson, and this has now been followed by a companion volume in French by the same author.

In each case the same plan has been adopted. In addition to the usual chemical terms, there is a general vocabulary of common words of most frequent occurrence, so that reference by a beginner to a second dictionary is largely obviated. In both dictionaries the basis and development of chemical nomenclature in the respective languages is concisely explained, so that it is usually possible to find the corresponding English equivalent, even when the actual word is not given.

Students only slightly acquainted with French chemical literature are frequently puzzled by the common use of colloquial or archaic words instead of the modern chemical terms, such as, for example, *sel de Seignette*, *sel de prunelle*, *sel diuretique*, etc. In translating these and similar terms the author of these dictionaries has usually given both the literal English equivalent and the chemical name of the compound, although there are a few exceptions to this useful rule, such as, for example, *eau de Labarraque*, and some omissions. In like manner, the composition of many pharmaceutical preparations is indicated in brackets after the translation, and the names of the various herbs associated with pharmacy are included, together with the more common medical terms.

The author must be congratulated upon having compressed so much into so small a space, and this French dictionary may be as warmly recommended to chemical students as its German predecessor.

Both books are bound in flexible covers of a size convenient for the pocket, and are clearly printed on good paper. EDITOR.