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THE ANALYST

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

Crayon Portrait of Dr. A. H. Hassall.

A PHOTOGRAPHIC reproduction of a crayon portrait of Dr. Arthur Hill Hassall, drawn in 1853 by J. N. Harland, is published with this issue of THE ANALYST.

The original drawing, which measures about 30 by 24 inches, has been presented to the Society by Dr. Hassall's colleague and medical attendant at San Remo, Michael Foster, Esq., M.D., F.R.C.P., to whom a cordial vote of thanks has been voted by the Council.

Arthur Hill Hassall was born in 1817 and died in 1894, and his obituary notice was written by Otto Hehner (see ANALYST, 1894, **19**, 97). He was the first Vice-President of the Society of Public Analysts.

The Institute of Chemistry has kindly allowed this portrait to be hung in one of its rooms.

The Identification of Apiol.

BY JOHN KING, F.I.C.

THE identification of commercial "apiol" is attended by some little difficulty, owing to its variable composition and the lack of reliable information as to the nature of different varieties at present on the market. I have not been able to discover in the existing literature any method which will detect commercial apiols with certainty, and have concluded that a Zeisel determination, carried out on the lines indicated later, is of greater value than any other factor in distinguishing apiol from other naturally occurring oils.

Hilditch and Jones (*J. Soc. Chem. Ind.*, 1927, **46**, 174T.) and Walmesley (*Quart. J. Pharm.*, 1928, **1**, 388) have recently published work elucidating many difficulties on the subject, and the latter has given a large number of analytical data showing plainly what great differences may be met with in commercial apiols. The analytical constants usually associated with oil analysis, such as specific

gravity, specific rotation, saponification value, etc., are certainly useful, but not quite diagnostic. L. Lutz and G. Oudin (*Ann. Falsif.*, 1910, 295, 335) have suggested analytical limits for different varieties of apiol, together with special tests depending on the action of nitric acid or a mixture of nitric and sulphuric acids on the substance. I have investigated these acid tests and consider that, quite apart from the personal danger in carrying out the tests by this method, the results are apt to be misleading.

The red colour developed on the addition of concentrated sulphuric acid to a few drops of apiol, as described by the British Pharmaceutical Codex and by the French Codex, 1908 edition, is by no means diagnostic, and may, in fact, be quite misleading. Many oily plant extracts will give various shades of red or brown with concentrated sulphuric acid, and in order that the test may be of value, the colour at great attenuation should be compared as to its red component with that given by known specimens. As the colour is affected by the absorption or addition of water, the attenuation should be made with concentrated sulphuric acid. A specimen of German parsley seed oil gave a distinctly red colour at a dilution of 1:30,000, as did also a specimen of Merck's white crystalline apiol. Other specimens of apiol gave somewhat less colour and some very much less. Comparative measurements of the colour produced by several commercial articles were made, in which 0·033 grm. of the apiol was treated with 10 ml. of concentrated sulphuric acid in the cold and stirred until homogeneous. Part of this was then diluted with strong sulphuric acid until a concentration of 1:7,500 was attained, and tests were carried out immediately by means of the Lovibond tintometer, the liquid being contained in a half-inch cell. It was necessary to do this as soon as mixing was complete, as the colour changed on standing, partly owing to absorption of moisture. One specimen, for example, increased its red index number threefold on standing 24 hours. The results, which are given in the table which follows, show how great were the differences of various specimens in colour-producing power.

The absorption spectrum of the colour produced by sulphuric acid may be of service in some cases. The colour showed no definite absorption bands. In specimens, such as Merck's, practically the whole of the absorption occurred at the violet end of the spectrum. Other specimens gave most absorption in the violet region, accompanied by varying amounts in the yellow and green regions. An attentuation in sulphuric acid of about 1:10,000 was found to be the most generally useful.

The rotation of polarised light may give useful negative information at times, but usually that of genuine specimens is so small and the colour so intense that reliable figures are not available. Merck's apiol gave a slight negative reading, and a German parsley seed oil a pronounced negative reading. Chemically pure apiol is optically inactive.

Few oils have a specific gravity greater than unity, the principal commercial ones being those derived from parsley, sassafras oil, and those containing eugenol-like bodies, such as oil of cloves. Unfortunately, some of these oils contain

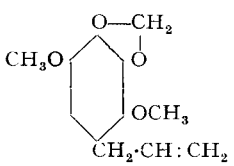
substances having methoxyl groups, the significance of which will be dealt with later, though their odour could hardly be mistaken for parsley derivatives.

Many naturally occurring oils fall within the refractive index range of 1·480–1·537 reported for apiol, but the refractive index may be useful as a confirmatory test; it has the advantage of requiring very little material. Several other oils containing methoxyl groups, such as matico, dill, elemi, asarum, bay, fennel, arnica and calamus, have refractive indices falling within these limits, and their possible presence should not be lost sight of. Sea fennel oil, for example, contains nearly half its weight of dill apiol, though its specific gravity is somewhat low and it has a strongly positive rotation. The saponification value will show the presence of esters, including, of course, glycerides.

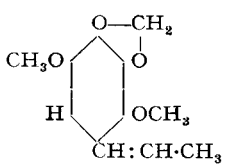
It occurred to me, from a study of the chemical constitution of the substances reported to have been found in apiol, that a more diagnostic constant than any hitherto described would be a Zeisel number, that is, the proportion of volatile iodide obtainable by treatment with hydriodic acid. Furthermore, only, 0·1–0·2 grm. would be necessary, since good specimens give about double their weight of silver iodide. This is a very great consideration when only a few drops contained in gelatin capsules are available, as is often the case in chemico-legal work. The methoxyl content alone cannot be considered to be quite diagnostic, as other naturally occurring substances (including some other essential oils) would give fairly high figures, but these substances are, as a rule, easily differentiated from those of similar composition to apiol. Thus, alcohols (including glycerol), esters (including glycerides), ethers, (including bodies like β-naphthol methyl ether), and other substances contained in some of the well-known essential oils, would possibly give iodine compounds of sufficient volatility to rank as methoxyl-containing compounds under the conditions given later. Generally, the presence of these substances could easily be detected by odour, saponification value, refractive index and specific gravity, and some, such as the glycerides, contribute only a small proportion of iodide. If necessary, some of them could be eliminated by saponification, followed by extracting with low-boiling petroleum spirit the substance required for hydriodic acid treatment.

The composition of apiol and related bodies is as follows:—

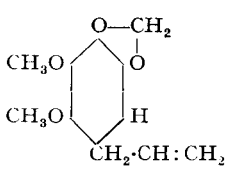
Apiol



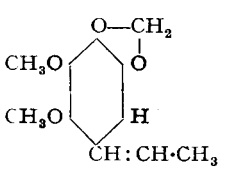
Iso-apiol

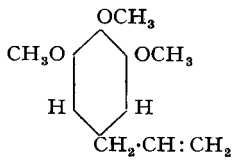


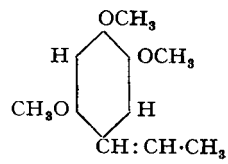
Dill apiol

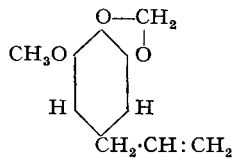


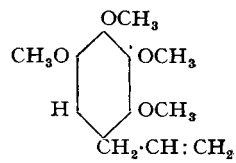
Dill iso-apiol



Elemicin 

Asaron 

Myristicin 

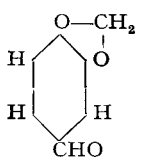
Allyl tetramethoxybenzene 

Apiol, myristicin and allyl tetramethoxy-benzene have been found in commercial apiols. Dill apiol has been found in dill oil, elemicin in elemi oil, and asaron in calamus and matico oils.

It may be of interest here to give a list of the principal products from which a fair yield of silver iodide would be given by the Zeisel method:—Apiol, dill, matico, sea-fennel, fennel, elemi, asarum, calamus, cassia, betel, bay, cloves, nutmeg, ylang-ylang, arnica, vanilla, and yara-yara.

The action of hydrogen iodide on glycerides at high temperatures is known to be that of splitting up the molecule, giving eventually isopropyl iodide. There is nothing in the literature, however, to indicate to what extent this goes on quantitatively, and, in view of the large glyceride content of some commercial specimens of apiol, it was necessary to investigate this point under the conditions given later. Pure triolein was chosen for the glyceride, and it was found that only about 50 per cent. of the theoretical yield of silver iodide was obtained under the conditions specified; and this, in view also of the high molecular weight of glycerides, rules out the possibility of glycerides seriously disturbing the results obtained by the modified Zeisel method. The use of alcohol in the preparation of apiol from parsley seed should be borne in mind and a test should be made for its presence.

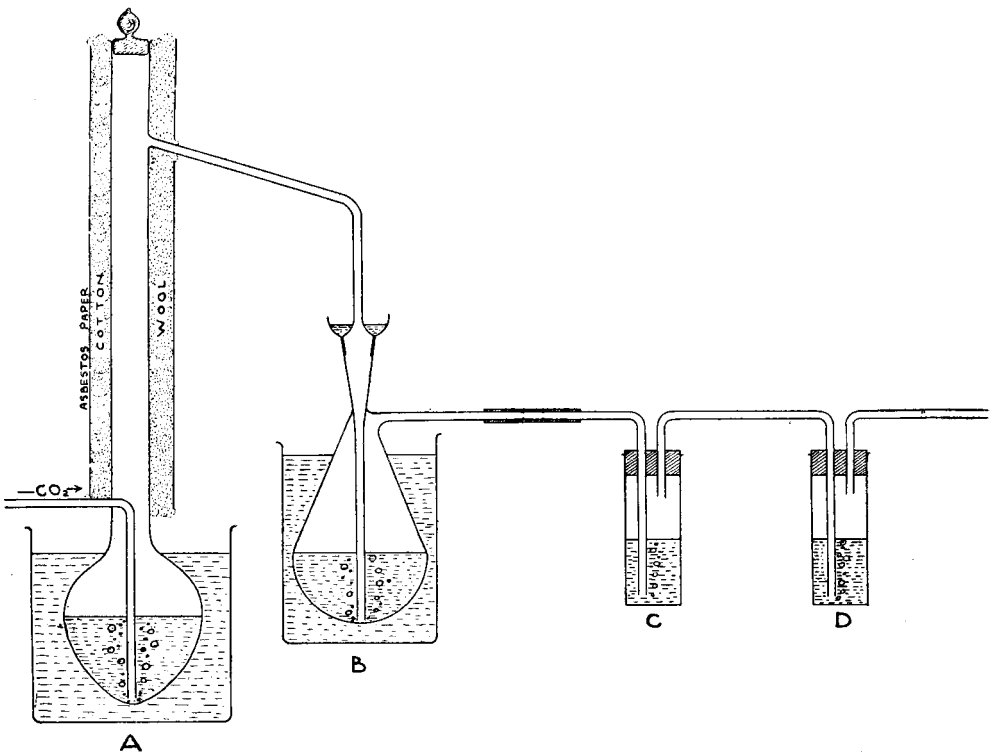
It was also necessary to study the action of hydriodic acid on substances containing the methylene-oxy group which is contained in apiol and related bodies, apart from the action on methoxyl groups. For this purpose piperonal



was chosen, and treated with hydriodic acid under the conditions given in the experimental portion. No iodine compound of sufficient volatility under the conditions of the experiment passed into the absorption tubes, which was rather surprising in view of the possibility of methylene iodide being formed and passing over. This was also confirmed by the action of hydriodic acid on Merck's pure

crystallised apiol, which gave a yield somewhat less than that calculated from two methoxyl groups, no volatile compound having come from the methylene-oxy group.

METHOD USED IN DETERMINING RELATIVE METHOXYL GROUPS.—The apparatus used was a modification of the usual Zeisel apparatus designed by L. V. D. Scorah, M.Sc., A.I.C., for use in the determination of glycerin, and described now with his kind permission. It has the advantage of employing ground glass joints in all places where iodine, hydriodic acid or organic iodine compounds may come in contact with the joint. Carbon dioxide is used to sweep along the products of decomposition into the absorption tubes, and the bulbs are blown in such a way as to ensure the maximum of disturbance consistent with slow gas-bubbling.



The oil under examination was weighed in suitable quantity into an open glass capsule, and lowered by means of a wire into the bulb A; 20 ml.. of 57 per cent. (by weight) hydriodic acid, of constant boiling point, were then added, and a slow stream of carbon dioxide, purified by bubbling through a wash-bottle containing sodium carbonate solution, was passed through the apparatus. The rate of flow was regulated to about three to five bubbles per second. Tubes C and D contained a few ml. of 10 per cent. alcoholic silver nitrate solution. The bulb A was surrounded by a glycerin bath and heated to 140° C. during the experiment. The

bulb B contained red phosphorus suspended in water and was surrounded by a water-bath kept at 70° C. The reaction was usually complete in about 60 minutes, as was shown by the absence of precipitate in a fresh tube of silver nitrate replacing those taken away at C and D after this time had elapsed. After evaporation of the alcohol, boiling water and a little dilute nitric acid were added, and the silver iodide filtered and washed on a Gooch crucible in the usual way. A blank always preceded a series of experiments and did not exceed a mgrm. or so of silver iodide.

RESULTS WITH COMMERCIAL APIOLS.—Several commercial apiols from different sources were tested under the above conditions, and the results are embodied in the table which follows. The piperonal and pure triolein, referred to above, were also treated under the same conditions.

Origin.	Character.	Sp. Gr. 15°/15°C.	Refract. Index. n_D^{20}	Rotation 20°C.	Saponification value.	Zeisel value expressed as wt. of (CH_3O) from 1 grm. of material.	Colour on Lovibond's tintometer scale at dilution of 1:7,500, in ½ inch cell. Read immediately. Red.	Yellow.	Read after 20 hours. Red.	Yellow.
German "Merck's white crystalline"	White crystals m.pt. about 30° C.	1·175	1·5370	−0° 6′	7·7	0·2582	7	5	Unreadable	
French "apioline"	Slightly yellow liquid: no crystals on standing	1·133	1·5328	—	7·0	0·2675	4	8	12	10
French "apiol"	Thick green oil	0·9729	1·4840	—	175	0·0256	0·4	0·4	0·7	1·0
English "apiol"	Green oil: no crystals on standing	1·0606	1·5080	—	67·0	0·2386	2·0	9·5	5·0	13
" "	Thick green oil depositing crystals on standing	1·036	1·5005	—	117·7	0·1190	3·0	4·5	3·0	9
German "Parsley seed oil"	Slightly yellow: liquid no crystals on standing	1·0713	1·5260	−7° 0′	8·0	0·0712	11	9·6	Unreadable	
Unknown	Green oil	1·012	1·4989	—	—	0·0781	Not available			

CONCLUSIONS.—Merck's specimen was not quite pure, as shown by lack of sharpness in melting point, slight optical activity and saponification value. The Zeisel value was somewhat below that demanded by theory, though it is possible that a 100 per cent. yield of silver iodide is not realisable. The French "apioline" gave an almost theoretical result for the Zeisel value of pure apiol, though this was probably fortuitous, since myristicin and tetramethoxyl allyl benzene might, in suitable proportion, give this Zeisel result and were both probably present. The so-called French "apiol" obviously contained little or no methoxyl constituent, being, in fact, an almost pure glyceride. Triolein gave a Zeisel value only slightly below this specimen, although the colour test carried out according to the B.P.

Codex was satisfactory. The tintometer test at great dilution indicated almost total lack of specific colour-producing substance, showing how misleading the old colour tests may be. The high viscosity and ready solubility in 90 per cent. alcohol of the French "apiol" indicated gross adulteration with castor oil.

The first of the English apiols contained probably one-third of its weight of glyceride, judging from its saponification value. The Zeisel value was higher than would be accounted for by assuming the remaining two-thirds to be pure apiol, indicating the presence of a tri- or tetra-methoxy compound.

The second of the English apiols contained more than one-half of its weight of glyceride. The Zeisel value bore approximately the same relation to the non-glyceride portion as was found in Merck's pure apiol or the French "apioline."

The last two specimens were distinctly low in methoxyl content, and the low saponification value points to their being distilled rather than extracted oils. The German parsley seed oil gave a very high colour figure, showing little agreement with the methoxyl content. The colour was actually a good deal higher than Merck's specimen, whereas the Zeisel value was less than one-third. In view of this, it is evident that the colour test with sulphuric acid, particularly at low dilutions, does not have the value usually ascribed to it.

SUMMARY.—The methods hitherto employed in the examination of apiol have been applied to certain commercial samples.

An improved method of carrying out the sulphuric acid test, employing the Lovibond tintometer, has been described. It has been concluded that the methoxyl content, determined by a modified Zeisel process, is the most distinguishing criterion, in conjunction with various physical data.

I wish to thank the Government Chemist for permission to publish this work.

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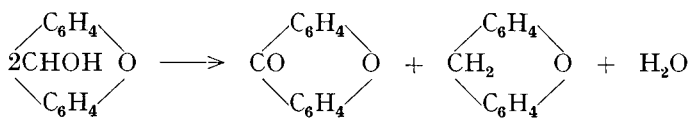
The Preparation and Properties of Xanthydrol as a Reagent for Urea.

By F. G. KNY-JONES, B.Sc. and A. M. WARD, B.Sc., Ph.D., A.I.C.

Xanthydrol is a sensitive reagent for the detection and determination of urea (see R. Fosse, "L'uree. (*Recherches de chimie analytique, biologique et agricole.*) Les fonctions dixanthopyranol, xanthydrol et sel de pyryle." Paris, 1928). It is, however, so unstable that alleged specimens are often only the decomposition products (xanthone and xanthane), which do not give condensation products with urea. Commercial specimens of xanthydrol accordingly may fail to detect the presence of urea.

Xanthydrol was prepared by reducing xanthone, the latter being readily obtained by distilling salol, as described in *Organic Syntheses* (Vol. VII, p. 84). The product, consisting of pale yellow needles, was extracted under a reflux condenser with small quantities of acetone until the extracts, which were at first yellow, became colourlesss. The solid remaining was then dissolved in acetone (moderately soluble in the hot solvent), giving a colourless solution, from which xanthone crystallised in colourless needles, m.pt. 174° (uncorr.). A further quantity of pure xanthone may be obtained from the various liquors. Xanthone has previously been prepared colourless by Dhar (*J. Chem. Soc.*, 1916, **109**, 745) by repeated crystallisation from acetic acid or nitrobenzene.

The reduction of an alcoholic suspension of xanthone was carried out by means of sodium amalgam (*Organic Syntheses*, Vol. VII, p. 88; Fosse, *op. cit.*, p. 287), and this method appears to be entirely satisfactory. Drying the product at 40–50°, however, as described in *Organic Syntheses*, usually resulted in complete decomposition, mainly to xanthone and xanthane:



together, possibly, with some dixanthydryl ether. Xanthydrol was accordingly filtered off from the suspension obtained by pouring the alcoholic solution into water. (The aqueous filtrate from the xanthydrol always became turbid after acidifying, and the white emulsion, which slowly turned pink, solidified on standing. *o*-Phenoxybenzoic acid, m.pt. 113°; mol. equivalent, by analysis of silver salt, 216; calc., 212, was obtained from this.) The xanthydrol was rapidly dried on a porous saucer at room temperature, and at once used, or else kept dissolved in ethyl alcohol until required. It was frequently found that a specimen of xanthydrol, dried at room temperature, had undergone almost complete decomposition at this temperature after a few days. The alcoholic solution is much less prone to decomposition, and such a solution after keeping for 3 months still gave a

copious precipitate with an aqueous solution of urea and glacial acetic acid (compare Fosse, *op. cit.*, p. 10).

The melting point of 120–123° C. for xanthydrol, given in *Organic Syntheses*, was sometimes observed, but the m.pt. is dependent upon the conditions of heating, since xanthydrol decomposes above its m.pt., mainly into dixanthydryl ether (m.pt. about 200°, Meyer and Saul, *Ber.*, 1893, **26**, 1276). No mention is made in *Organic Syntheses* of this decomposition, but it is quite definite. Thus the temperature of a specimen of xanthydrol in a capillary tube was slowly raised from room temperature; melting began at 117° C., and was practically complete at 123° C.; bubbles then rose through the liquid (135–140° C.), and the material began to resolidify at 140° C. The colourless solid again softened at about 160° C., the main melting was above 190° C., and the temperature reached 201° C. before all had melted. A separate sample, plunged in the bath at 135° C., melted completely, decomposed, and re-solidified. Melting again commenced at about 190° C., and was complete at 198° C. Different experiments gave varying temperatures for these phenomena, but the general behaviour was in all cases as given above. Melting-point determinations of this compound, therefore, afford little criterion of purity, and the homogeneity of the product was checked by the condensation of its alcoholic solution with aqueous urea in the presence of glacial acetic acid, as described by Fosse; if the solution, after separation of the condensation product, gave no precipitate or only a slight turbidity on pouring into water, the initial material was judged to be xanthydrol only. (In some experiments, a small precipitate was thrown down on pouring the solution into water, but this was found to be the urea condensation product.)

In using xanthydrol for the detection or determination of urea, it therefore seems best to prepare this substance immediately before it is required by reducing xanthone, which is quite stable, by means of alcoholic sodium amalgam. The alkaline alcoholic solution is poured into excess of water, the product filtered off, washed, partly dried at room temperature, and re-dissolved in alcohol. A methyl or ethyl alcoholic solution of xanthydrol appears to be much more stable than the solid; it seems useless to attempt to keep the solid, even at room temperature, under ordinary conditions for any length of time.

One of us (A.M.W.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the materials.

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Electrometric Determination of Copper.

II. APPLICATION OF VOLHARD'S METHOD TO ELECTROMETRIC ANALYSIS.

By MARJORIE E. PRING, M.Sc., and
JAMES F. SPENCER, D.Sc., Ph.D., F.I.C.

In 1878 Volhard described a method for the volumetric determination of copper (*Annalen*, 1878, **190**, 1). In this method the solution of a copper salt, after being made neutral, was saturated with sulphur dioxide, raised to the boiling point and treated with a measured excess of a standard solution of potassium thiocyanate. When cold, the solution was filtered from the precipitated cuprous thiocyanate and an aliquot portion of the filtrate titrated with standard silver nitrate solution, using a nitric acid solution of a ferric salt as indicator.

Since it has been shown by Behrend (*Z. physikal Chem.*, 1893, **11**, 476) that a solution of thiocyanate may be titrated electrometrically by silver nitrate, using a silver electrode coupled with a calomel half-cell, it appeared possible that the methods of electrometric titration could be applied to Volhard's process. Further consideration indicates that the process may be simplified. It is obvious that, in the method as originally put forward, the cuprous thiocyanate must be removed before titration with silver nitrate.

Before proceeding to examine the titration of copper salts it was necessary to ascertain that the sulphur dioxide can be entirely removed from the solution by a moderate amount of boiling, for should any remain in the solution, since it is neutral, silver sulphite would be precipitated. To settle this point, a solution of potassium thiocyanate was titrated with silver nitrate and a similar solution was saturated with sulphur dioxide, boiled until the odour of the gas had disappeared, cooled and titrated electrometrically.

The titration was carried out as described previously (Analyst, 1929, 509), using a silver plate and a 0·1 *N* calomel electrode. Since silver salts are being used, it is necessary to interpose a "salt bridge" between the titration vessel and the calomel electrode. The cell actually measured is represented by the scheme:

Ag | KCNS | *N*. KNO_3 | 0·1 *N* calomel electrode.

The results of the two titrations are given in the table.

Titration of 10 c.c. 0·1 *N* KCNS + 100 c.c. H_2O untreated with SO_2.		Titration of 10 c.c. 0·1 *N* KCNS + 100 c.c. H_2O after treatment with SO_2.	
0·1 *N* $AgNO_3$ added. c.c.	Voltage.	0·1 *N* $AgNO_3$ added. c.c.	Voltage.
1·42	+0·014	0·00	+0·051
3·00	+0·008	1·31	+0·030
4·52	+0·005	2·82	+0·021
5·90	±0·000	6·20	+0·014
6·94	−0·006	7·05	+0·001
7·96	−0·011	9·05	−0·025
8·87	−0·028	9·16	−0·030
9·04	−0·032	9·28	−0·040
9·20	−0·038	9·33	−0·049
9·34	−0·051	9·38	−0·055
9·42	−0·060	9·43	−0·067
9·46	−0·082	9·48	−0·089
9·53	−0·132	9·53	−0·121
9·57	−0·138	9·62	−0·123
9·73	−0·143	9·76	−0·128
10·05	−0·161	9·86	−0·133
End-point 9·50 c.c.		End-point 9·50	

These figures, as will be shown later, prove that the sulphur dioxide can be removed from the solution without undue boiling and that the change of E.M.F. at the end of the titration is sufficiently great to make the end-point easy of determination.

TITRATION OF SOLUTIONS OF COPPER SALTS.—Ten c.c. of a 0·2 *N* solution of copper sulphate were saturated with sulphur dioxide, 20 c.c. of 0·1 *N* potassium thiocyanate solution were added, and the solution boiled until the sulphur dioxide had been expelled. The precipitated cuprous thiocyanate was white. Water (150 c.c.) was added, and the solution left until cold. A silver plate and a 0·1 *N* calomel electrode were inserted, the latter through a potassium nitrate bridge, and the excess of thiocyanate was titrated with 0·1 *N* silver nitrate. The E.M.F. of the titration cell was read after each addition of silver nitrate, and the quantity of silver nitrate was plotted against the voltage, and a titration curve drawn. An example of such a curve is shown in Fig. 1, from which it can be seen that the E.M.F. falls rapidly at the commencement of the titration; it then remains almost stationary until within a few cubic centimetres of the end-point, when it falls rapidly. The end-point is fairly well marked, but it may be found more exactly by plotting the rate of change of E.M.F. with changing amount of silver nitrate, $\frac{\Delta E}{\Delta C}$, against the volume of silver nitrate added, as shown in Fig. 2. The end-point can be made sharper if no water is added other than that necessary to rinse the tube by which the sulphur dioxide is led into the solution. The type of curve

obtained in such circumstances is seen in Fig. 3, in which the change of E.M.F. at the end-point is well marked, and from which the titre can be read directly.

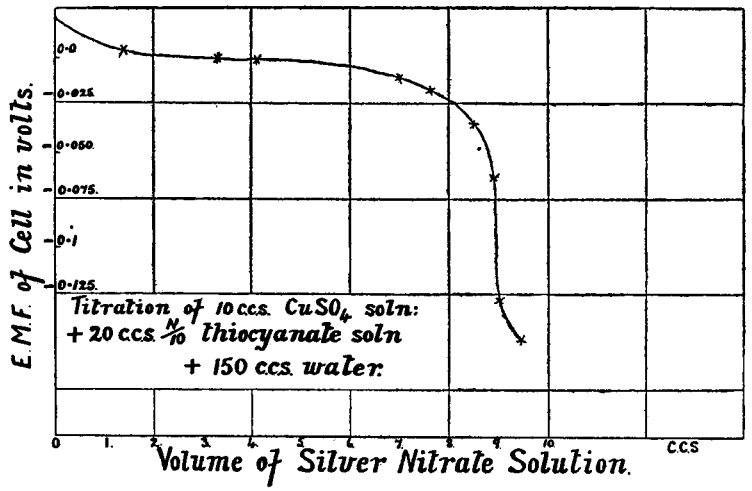

Fig 1.

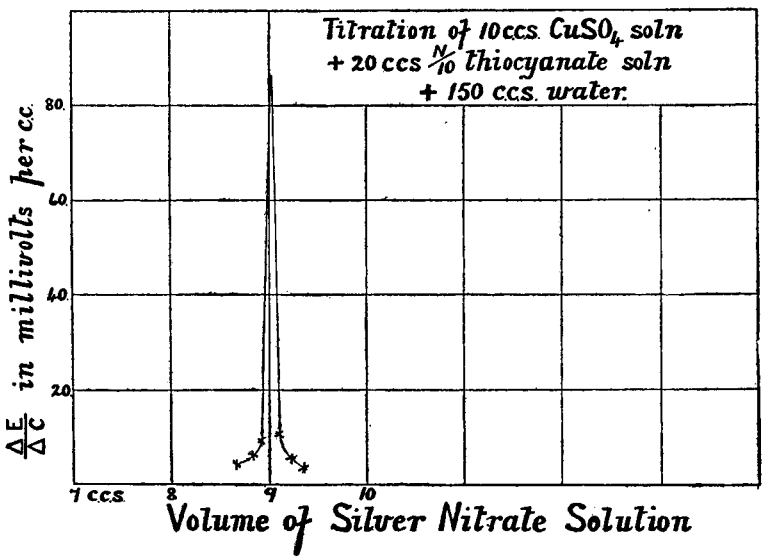

Fig 2.

To obtain such a sharp end-point it is necessary that the titration should be finished slowly, for the E.M.F. takes a little time to become steady as completion is approached.

EFFECT OF DILUTION OF THE COPPER SOLUTION.—The previous experiments have shown that the end-point of the titration becomes less sharp the more dilute the copper solution. Therefore to ascertain the limit of dilution permissible for accurate determination, solutions of 0·04 N and 0·02 N were treated with excess of 0·02 N and 0·01 N potassium thiocyanate solution, respectively, and the excess

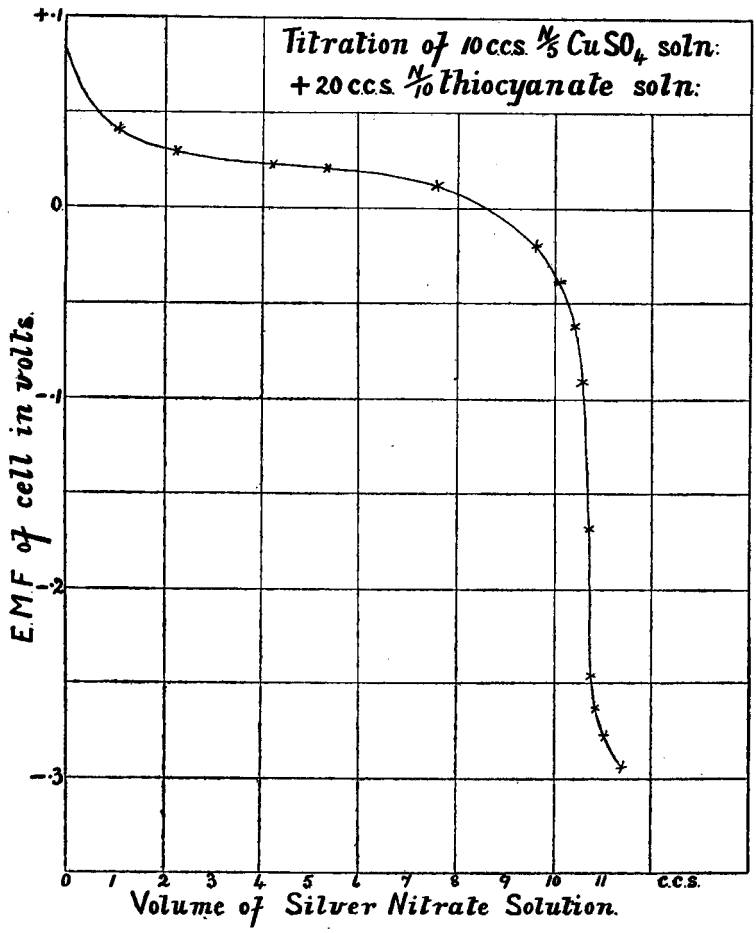

Fig. 3.

titrated with an equivalent solution of silver nitrate. The end-point was much less sharp with the more dilute solution. In the case of the 0·04 N solution the change of E.M.F. is not very marked at the end-point, but it is sufficient (Fig. 4) to allow the titration being carried out, whilst with the 0·02 N solution the end-point could not be deduced from the titration curve. Consequently, to obtain a satisfactory end-point, the copper solution must have a concentration greater than 0·04 N, and it must not be diluted other than by the reagents.

ACCURACY OF THE METHOD.—To define the accuracy of the method, several series of titrations were carried out with carefully standardised solutions of copper sulphate. The solutions were prepared from accurately weighed quantities of pure material, and the concentration of the solution was checked by electrolysis. Silver nitrate solutions were made from the pure salt and checked by titration with standard sodium chloride. The solutions of potassium thiocyanate were standardised by means of silver nitrate solutions and the titration was carried out as described above. The table gives the data of a series of measurements.

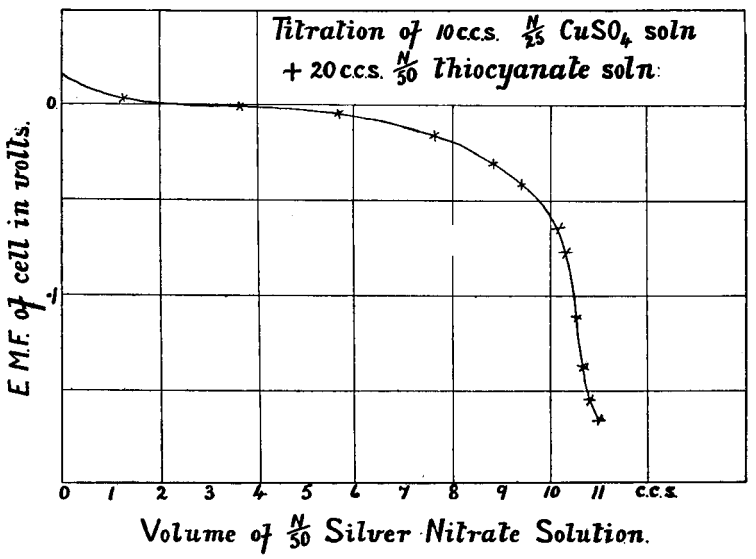

Fig. 4.

10·06 c.c. $CuSO_4$ 0·2002 *N* + 20 c.c. KCNS 0·09634 *N* + 100 c.c. H_2O titrated with 0·1027 *N* $AgNO_3$.

$AgNO_3$. c.c.	Voltage.	$AgNO_3$. c.c.	Voltage.	$AgNO_3$. c.c.	Voltage.	$AgNO_3$. c.c.	Voltage.
5·99	+0·018	6·17	−0·025	6·01	−0·010	5·90	+0·011
6·90	0·021	7·22	−0·006	6·95	±0·000	7·03	0·015
7·97	0·039	8·05	+0·002	7·90	+0·005	7·91	0·021
8·20	0·042	8·34	0·013	8·19	0·021	8·20	0·025
8·48	0·051	8·61	0·030	8·43	0·030	8·50	0·032
8·60	0·058	8·71	0·039	8·66	0·040	8·71	0·050
8·70	0·062	8·81	0·052	8·78	0·052	8·81	0·064
8·80	0·072	8·86	0·061	8·90	0·075	8·88	0·079
8·90	0·090	8·91	0·080	8·95	0·090	8·93	0·102
8·96	0·130	8·97	0·113	9·00	0·130	8·98	0·127
9·00	0·141	9·03	0·125	9·05	0·149	9·04	0·132
9·11	0·146	9·10	0·130				
End-point 8·94		End-point 8·94		End-point 8·96		End-point 8·94	

The average titre of the copper sulphate solution from the values above is 8·95 c.c., whilst the calculated titre has the same value.

In a further series of titrations 9·97 c.c. of $CuSO_4$ 0·03995 *N* were treated with 19·96 c.c. of KCNS, 0·1038 *N*, and the excess thiocyanate titrated with $AgNO_3$ 0·09856 *N*. In four successive experiments the volume of silver nitrate required was 10·89, 10·91, 10·91 and 10·90 c.c., respectively. This gives an average titre of 10·90 c.c., whilst the calculated value is 10·91 c.c. From the foregoing results it is clear that the agreement between the calculated titre and the experimental value is very close, both for 0·2 *N* and 0·04 *N* solutions of copper sulphate. It has already been shown that solutions more dilute than 0·04 *N* do not yield a satisfactory end-point.

INFLUENCE OF ZINC AND IRON ON THE ACCURACY OF THE METHOD.—In the course of analysis of copper-containing materials, iron and zinc are frequently found, and in such cases it would be very convenient if the copper could be determined in the presence of these metals. Consequently it was decided to ascertain whether the presence of iron and zinc has any effect on the accuracy of the method described. A solution of copper sulphate of approximately 0·2 *N* was diluted with an equal volume of water, 0·1 *N* zinc sulphate, and 0·1 *N* ferric alum, respectively; 10 c.c. of each of the mixtures were treated as described above, and the excess of thiocyanate titrated with silver nitrate. The results are given in the table below for a series of four titrations in each case.

Volume of $AgNO_3$ solution required.

$CuSO_4$ alone.	$CuSO_4 + ZnSO_4$.	$CuSO_4 + Fe_2(SO_4)_3$.
c.c.	c.c.	c.c.
10·72	10·73	10·72
10·71	10·72	10·70
10·74	10·73	10·69
10·71	10·73	10·73
Mean 10·72	Mean 10·73	Mean 10·71

From these figures it is clear that the divergence from the value obtained with solutions of copper sulphate alone is 0·01 c.c., or less than 0·1 per cent., indicating that the method described is accurate in the presence of either iron or zinc.

CONCLUSION.—Copper may be determined electrometrically in neutral solutions of concentrations down to 0·04 *N*, *i.e.* 1·25 grms. of copper per litre, by saturating the solution with sulphur dioxide, then precipitating cuprous thiocyanate with a measured excess of standard potassium thiocyanate, boiling the solution and, after cooling, titrating the excess thiocyanate with standard silver nitrate. Since the method does not involve filtration of the cuprous thiocyanate, it is both more rapid and more accurate than titration in the presence of a coloured indicator. The determination may be carried out in the presence of iron or zinc salts without diminution of the accuracy.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research which enabled one of us (M. E. P.) to take part in this work.

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The Determination of Small Amounts of Nickel in Steel.*

By B. JONES, B.Sc., A.I.C.

The determination of nickel in steel is usually carried out by precipitation with dimethylglyoxime or α-benzildioxime in slightly alkaline solution, and treating the precipitate so obtained gravimetrically or cyanometrically. This is a widely-practised method and is excellent when there is sufficient nickel in the steel to yield a precipitate which may be weighed or titrated with accuracy. When, however, the nickel content is less than 0·06 per cent., tests have shown that it is questionable whether the small amounts of this metal are completely precipitated even after a prolonged stand, and whether the determination of nickel in the precipitate is accurate when working on the usual quantity of material. The following small amounts of nickel were taken, and precipitated with dimethylglyoxime in slightly ammoniacal solution in a volume of 100 c.c., and allowed to stand over-night, they were then filtered through a close pulp filter, the precipitate was not washed, and the filtrates were examined for the presence of nickel by the method described later.

Weight of nickel taken, grm.:—	0·0001	0·0002	0·0003	0·0005	0·00075	0·0010	0·0015	0·0020	0·0025
Percentage of total nickel found in filtrate:—	35·0	7·5	5·0	2·0	2·0	2·25	1·0	0·25	Negligible

Difficulties from the above source may be partly surmounted by working on a large weight of sample in order to obtain a larger precipitate, but in certain circumstances large quantities of material are not always available. It appears to be the general procedure with many chemists to report small amounts of nickel in steel as "traces" when there is just sufficient of the element to give a precipitate, after long standing, with the reagent too small for quantitative measurement. In fact, less than 0·1 per cent. is often registered as "traces." When a definite figure is requested, as in the analyses of standard steels, reports from analysts differ as widely as for any element. Thus nickel figures reported by experienced analysts for British Chemical Standard Steel A2 vary from 0·030 to 0·078 per cent., a difference of 160 per cent. While these small amounts of nickel as yet seem to have no appreciable effect upon the mechanical properties of steel, yet from an analytical standpoint the position seems to be in rather an unsatisfactory state, and there appears to be room for a new method which will give a more quantitative significance to these small amounts. A similar position existed with regard to small amounts of chromium until fairly recent years (Evans, ANALYST, 1921, **46**, 38, 539).

* Communication from the Research Department, Woolwich.

The method proposed is a colorimetric one, and depends upon the reddish-brown colour given by the action of an oxidant upon the dimethylglyoxime complex of nickel. Mention should be made that Feigl (*Ber.*, 1924, **57**, 758) obtained a reddish colour by the use of peroxide of lead as the oxidant, but a disadvantage in the use of the latter is that the application of heat and a filtration are necessary. Rollet (*Compt. rend.*, 1926, **183**, 212) suggested the use of bromine to replace the oxidant used by Feigl (*vide supra*), and applied it to the determination of nickel in a variety of substances; he gives no figures, however; his claims regarding the quantitative separation of nickel from other elements have not been confirmed; and he ignores interfering elements. Under the conditions to be described, I have found that the employment of sodium hypochlorite as an oxidant gives very satisfactory results, and lends itself very well to colorimetric comparison with a standard. The method involves the isolation of nickel from large amounts of iron and its alloying elements as potassium nickelo-cyanide in ammoniacal solution, the iron, chromium, manganese, etc., being precipitated as hydroxides. This gives a very clean and quantitative separation of nickel from the main constituents of steel. Where, however, copper and cobalt also occur in more than small amounts, the chemical properties are so closely analogous to nickel that they interfere somewhat with the process, as they also form complex cyanides and modify the colour given by nickel. Fortunately it is rare to find the two metals as constituents of steel, and they can be dealt with as described later. Several well-known methods of separation of nickel from iron, such as the ammonium acetate and the zinc oxide methods, were attempted, but were discarded for various reasons. The filtrate from the precipitated hydroxides is used for colorimetric determination.

Method for Plain Carbon Steels.—One grm. is dissolved in 10 c.c. of hydrochloric acid, and oxidised with 5 c.c. of nitric acid. The solution is boiled for a few minutes and diluted somewhat with cold distilled water. It is then washed into a 200 c.c. standard measuring flask, diluted ammonia (1 part of 0·88 sp. gr. ammonia to 1 part of water) added from a burette or dropping bottle until a slight precipitate of hydroxide is formed which just fails to redissolve in the ferric chloride. Two c.c. of a 1 per cent. solution of potassium cyanide are now added and the flask well shaken, after which 10 c.c. of 1:1 ammonia are added, and the contents of the flask are made up to the mark with warm water. No allowance is made for the volume of precipitate. The whole is poured back into the original flask to mix the contents thoroughly, the precipitate is allowed to settle a little, and filtered off on a large fluted 41 Whatman filter paper, 100 c.c. of clear filtrate being used for the determination. A further 50 c.c. of filtrate are reserved for qualitative purposes, this being desirable, as, in my experience, all plain steels which are assumed to be almost free from nickel contain quantities far in excess of the amount for which the method was designed. The above method of separating nickel from iron is to be preferred to the one recommended in some text-books, of pouring the acid solution into ammonia containing cyanide, as it permits the nickel to react more readily with the excess of cyanide, and also keeps the quantity of

excess ammonia more under control. A large excess of ammonia should be avoided, as it is apt to interfere with the formation of potassium nickelo-cyanide and has a detrimental effect on the qualitative test. This is carried out as follows:—

APPROXIMATE DETERMINATION OF NICKEL.—The 50 c.c. of filtrate are cooled, transferred to a 100 c.c. Nessler glass, and diluted to the mark with water. Two c.c. of a clear solution of dimethylglyoxime in alcohol (just short of saturation) are added, the contents stirred with a glass rod, 1 c.c. of commercial sodium hypochlorite solution added, and the whole again stirred. The solution, on standing, will develop a reddish-brown colour if nickel is present, and is matched as follows:

Another 100 c.c. Nessler glass of the same size and bore is filled to the mark with water, six drops of 1 : 1 ammonia added, followed by 2 c.c. of dimethylglyoxime solution; the mixture is stirred, 1 c.c. of sodium hypochlorite added, and the liquid again stirred. Three drops of a standard nickel solution containing 0·00005 grm. per c.c. are run into the standard Nessler glass from a narrow 10 c.c. burette, and mixed. The colours are compared by viewing the glasses vertically over a white tile inclined at an angle to act as a light reflector, and the colour is matched by adding the standard solution, three drops at a time, and stirring after each addition, with intervals of several minutes between additions.

When the colour of the standard approaches that of the assay, additions must be made very cautiously. The colours of the two solutions may not be of exactly the same tint, owing to the interference of ammonium salts and decomposition products from the excess of cyanide added, which impart a brownish tint, but the amount of nickel registered by taking the reading when the intensity of colour of the solution is identical is nevertheless near to the truth.

The tint of the test solution improves on standing, and in some cases the qualitative figure is identical with the one finally obtained, although sometimes higher when the copper content is fairly large, but the interference of copper in the test is almost negligible when present in amounts usually found in steels, as any colour given is discharged by the potassium cyanide present in the filtrate.

Meanwhile, the main 100 c.c. filtrate are made just acid with hydrochloric acid, 5 per cent. of the strong acid is added in excess, and hydrogen sulphide is passed into the warm solution in a rapid stream for 15 minutes. Any copper sulphide (mixed with a little sulphur) is allowed to settle out on the water-bath, and when the precipitate has coagulated it is filtered through a pulp filter into a 600 c.c. wide-mouthed beaker and washed with a dilute solution of an electrolyte, such as 5 per cent. ammonium chloride.

Long standing is not necessary to remove the whole of the copper, as traces not precipitated have no effect on the determination; if it is known that only traces are present, this stage may be omitted. The filtrate is boiled down to low bulk, and then taken from the source of heat, and 50 c.c. of concentrated nitric acid added to destroy ammonium salts. A rather brisk ebullition occurs at this stage, and further heat is applied cautiously, the whole being taken to complete dryness, but

not baked for any length of time; further small additions of nitric acid may be necessary to complete the destruction of the ammonium salts. The residue is taken up with hot water, heated till it is dissolved, filtered, if necessary, and cooled.

COLORIMETRIC DETERMINATION.—It is now ready for colorimetric determination, either on the whole solution, or after being made up to a known volume, and a suitable fraction taken which will be indicated by the qualitative test. If the nickel content is very minute as shown by that test, another determination may be made *de novo*, starting with a 4 grm. sample, making the solution up to 500 c.c., and using half for the determination. A good working idea of the nickel content of the sample is obtained in about 45 minutes from the commencement of the experiment. For colorimetric measurement the solution should not contain more than 0·1 mgrm. of nickel, *i.e.* 2 c.c. of standard solution, or results will tend to be inexact, as it is difficult to determine the changes of tint with more concentrated solutions.

The colour reaction is very sensitive and will detect 0·01 mgrm. in 100 c.c. of solution, or 1 part in 10,000,000. It is a very stable colour, remaining almost of the same intensity till next day, thus ensuring an accurate comparison in a slow titration. There is usually no "blank" due to reagents.

The standard nickel solution in these experiments was made by dissolving 0·05 grm. of Hilger's spectroscopically standardised nickel in dilute nitric acid and making up to one litre.

TEST OF THE PROCESS.—Unsuccessful attempts were made to find a steel free from nickel. The fact that much more nickel is found in steels than in irons, suggests that the source of the nickel is from steel scrap used in the manufacturing process. Armco iron was also quite unsuitable for blank tests; even some electrolytic irons contained as much as 0·01 per cent. of nickel, but some specially deposited iron made in the Research Department, Woolwich, gave only 0·003 per cent., and this was used in the test experiments.

Sample analysed.	Weight taken. Grms.	Burette reading. c.c.	Weight of nickel. Grm.	Nickel. Per Cent.
Electrolytic iron A	4	1·20 × 2	0·00012	0·003
Electrolytic iron B	4	2·00 × 2	0·00020	0·005
*Electrolytic iron C	4	1·60 × 4	0·00032	0·008
*B.C.S. cast iron "B"	4	1·20 × 4	0·00024	0·006

* Final solutions made up to 200 c.c. and 100 c.c. taken.

Varying amounts of standard nickel solution were added to a solution of electrolytic iron A, and the following results were obtained. The rather large blank was unavoidable.

Weight of sample. Grms.	Nickel added. Grms.	Nickel added. Per Cent.	Burette reading. c.c.	Blank on E.1. c.c.	Net burette reading. c.c.	Nickel recovered. Grm.	Nickel recovered. Per Cent.
4	0·00005	0·0012	1·60	1·20	0·40 × 2	0·00004	0·001
4	0·00008	0·0020	2·00	1·20	0·80 × 2	0·00008	0·002
*4	0·00015	0·0037	1·30	0·60	0·70 × 4	0·00014	0·0035
*4	0·00020	0·0050	1·55	0·60	0·95 × 4	0·00019	0·0047
*4	0·00028	0·0070	1·90	0·60	1·30 × 4	0·00026	0·0065
1	0·00005	0·0050	0·80	0·30	0·50 × 2	0·00005	0·0050
1	0·00010	0·0100	1·30	0·30	1·00 × 2	0·00010	0·0100
*1	0·00020	0·0200	1·10	0·15	0·95 × 4	0·00019	0·0190
*1	0·00030	0·0300	1·55	0·15	1·40 × 4	0·00028	0·0280

* Final solutions made up to 200 c.c. and 100 c.c. taken.

The following plain carbon steels were analysed for nickel by precipitation with dimethylglyoxime on a 5 grm. portion, the precipitate allowed to stand overnight, and then treated cyanometrically. The result was compared with the figure obtained by the method under discussion.

Steel.	Precipitation and titration process. Per Cent.	This process. Per Cent.
1	0·011	0·024
2	0·021	0·030
3	0·023	0·042
4	0·040	0·048
5	0·057	0·060
6	0·070	0·072
7	0·082	0·083
8	0·150	0·153

The above results suggest that there is a solubility effect which comes into play in the precipitation method, which manifests itself rather strongly below a certain value, *i.e.* 0·06 per cent.; this shows that amounts of nickel below this figure require to be determined by another method.

ALLOY STEELS. EFFECT OF ALLOYING ELEMENTS ON THE PROCESS.—Tests were carried out to ascertain the effect of elements alloyed with iron; varying amounts of these elements were added to electrolytic iron A, and the filtrates were examined for the presence of the added elements.

Manganese.—One grm. portions of E.1 were dissolved as described, and amounts of reduced $N/10$ potassium permanganate added, after which the conditions of the process were followed. The filtrates were boiled to a small volume, nitric acid added, and the liquid taken to almost dryness, 30 c.c. of nitric acid (sp. gr. 1·2), added, and the manganese was determined colorimetrically.

$N/10$ $KMnO_4$ added. c.c.	Grm. of manganese.	$N/10$ $KMnO_4$ required.	
1	= 0·0011	<1 drop	
5	= 0·0055	<1 ,,	
7	= 0·0077	<1 ,,	
10	= 0·0110	1 ,,	
15	= 0·0165	<2 drops	
20	= 0·022	2 ,,	=0·1 c.c. =0·00011 grm. Mn.
30	= 0·033	4 ,,	=0·2 c.c. =0·00022 grm. Mn.
50	= 0·055	2·3 c.c.	=0·0025 grm. Mn.

It appears that, under the conditions described, the determination of nickel may be safely carried out in the presence of manganese up to 2 per cent. without interference. Higher amounts would interfere, owing to the formation of a brown colloidal peroxide with the sodium hypochlorite. High manganese steels are treated as described later.

Chromium, Molybdenum, Aluminium, Vanadium are all removed by ammonia.

Tungsten may be removed in the early stages as tungstic acid, but if the amount is small, filtration is unnecessary, as the tungsten is removed quantitatively in the iron precipitate, and the only way in which it interferes is that any separated tungstic acid somewhat obscures the neutralisation point before the potassium cyanide addition.

Copper and Cobalt, when present, appear to enter the filtrate quantitatively when there is sufficient potassium cyanide added to combine with them. Copper steels require no modification of the method described, the copper being removed with hydrogen sulphide, and no further excess of cyanide is necessary, as there appears to be a preferential formation of the nickelo-cyanide, whatever the copper content. Copper when present as a constituent is detected in the qualitative test by a pink permanganic colour with the reagents, which develops into a reddish-brown, and its presence intensifies the colour given by the nickel. This interference is overcome by the addition of 1 c.c. of the potassium cyanide solution, when the colour given by copper is nullified temporarily and the nickel content may then be judged. Cobalt is revealed in the filtrate by a yellow colour of the cobalti-cyanide.

The following experiment was carried out on 1 grm. portions of electrolytic iron A to which was added 0·0001 grm. of nickel and 0·02 grm. of cobalt; the potassium cyanide additions were varied, and nickel was determined in the filtrates as described for the qualitative test.

Potassium cyanide solution added. c.c.	Nickel recovered.
1	Nil
5	Nil
10	Trace after standing
15	1·7 c.c. = 0·000095 × 2 = 0·00017 grm

It appears that small amounts of nickel do not enter the filtrate quantitatively in the presence of much cobalt until there is an excess of cyanide added to combine with all the latter element first, after which the whole of the nickel enters the filtrate. The high result above is due to appreciable traces of nickel present in the standard cobalt solution. A blank test on the last experiment (no nickel added) was carried out, when 0·8 c.c. of standard nickel solution was required to match the colour obtained.

$\therefore$ 1·7 c.c.—0·8 c.c.=0·9 c.c. Net=0·00009 grm. of nickel.

MODIFICATIONS OF PROCESS IN PRESENCE OF ALLOYING METALS. HIGH MANGANESE STEELS.—The sample is dissolved in 30 c.c. of nitric acid (sp. gr. 1·2), evaporated to a small volume, and 50 c.c. of strong nitric acid added. The solution is cooled, and 5 c.c. of chloric acid added, after which it is boiled for 5 minutes and again cooled; a further 50 c.c. of strong nitric acid and 5 c.c. of chloric acid are added, and the solution is again boiled for 5 minutes. It is then filtered through asbestos, after cooling, a gentle suction being applied, and the precipitate is washed with strong nitric acid. This treatment, which is a modification of the Ford and Williams process, removes manganese as the peroxide, and avoids the addition of potassium salts, an excess of which interferes with the final colour given by nickel. The solution is transferred to a large wide-mouthed beaker and rapidly evaporated to a small volume, after which 10 c.c. of hydrochloric acid are added, and the solution boiled for a few minutes. The solution is now treated in exactly the manner described for plain steel.

COBALT STEELS.—Separation of cobalt from small amounts of nickel by means of α-nitroso-β-naphthol, after heating the filtrate with sulphuric acid until fumes appeared, was attempted, but was abandoned, as it gave low results for nickel. It was then decided to make a direct determination of nickel by keeping the cobalt in solution as the cobalti-cyanide. Sufficient potassium cyanide must be added to combine with all the cobalt and nickel present, and it is essential to know approximately the cobalt content of the steel. Thus for every 0·01 grm. of cobalt present, 5 c.c. extra of 1 per cent. potassium cyanide solution must be added. The yellow colour given by the cobalti-cyanide interferes when the amount of nickel is very low, and allowance must be made for it. This is done in a Walpole colorimeter. (ANALYST, 1925, **50**, 391.)

The filtrate is divided into two equal parts, the volume of these being indicated by the approximate test, and made up to 100 c.c., each in Nessler glasses. These two tubes, A and B, are placed in the upper compartment of the colorimeter, and immediately over two other tubes, C and D, respectively, in the lower compartment. The two latter contain six drops of 1:1 ammonia and the reagents, while the reagents are added to A. The contents of the tube D are now titrated with the standard nickel solution until a match is obtained, vertically through A and B. Copper does not interfere in this process, owing to the excess of cyanide in the filtrates which neutralises the effect of any copper, unless this is present in large

amounts, when it must be removed in the initial stages by treatment with hydrogen sulphide after dissolving the sample in hydrochloric acid.

The following results were obtained by adding small amounts of nickel to 1 grm. portions of electrolytic iron A, to which were also added elements as described.

Nickel added.		Metals added.			Blank.	Nickel recovered (on half quantity).		
Grm.	Per Cent.	Grm.		Per Cent.	Grm.	Gross. Grm.	Net. Grm.	Per Cent.
0·00005	0·005	Cr	0·20	20	0·000015	0·00004	=0·000025	0·005
0·00010	0·010	Cr	0·20	20	0·000015	0·00006	=0·000045	0·009
		Mo	0·01	1				
0·00010	0·010	Mn	0·20	20	0·000015	0·000065	=0·00005	0·010
		Cr	0·02	2				
0·00010	0·010	V	0·01	1	0·000015	0·000060	=0·000045	0·009
0·00010	0·010	Co	0·05	5	*0·000035	0·000065	=0·000030	0·012
		Cr	0·02	2				
0·00015	0·015	Cu	0·02	2	0·000015	0·000085	=0·00007	0·014
0·00020	0·020	W	0·10	10	0·000015	0·00011	=0·000095	0·019

* Nickel detected in cobalt added; half final solution taken.

Some results are appended which were obtained on various steels, including some British Chemical Standards.

Steel.	Percentage composition.	Results by other processes. Per Cent.	Results by this process. Per Cent.
Q 1	Mn 0·32	0·072	0·074
H R K 34	Mn 1·30	Traces	0·040
S D 2	Mn 1·14, Cr 0·013	Faint trace	0·040
U 2	Mn 0·32, Cr 0·09, W 6·15	0·140	0·144
Z S F C 2	Mn 0·76	0·062	0·065
Armco iron		0·058	0·060
B.C.S. cast iron "B"	Mn 0·63, C 3·06	Not reported	0·006
B.C.S. "P"	Mn 0·706	Traces	0·021
B.C.S. "V"	Mn 0·54, Cr 0·86, V 0·273	Traces	0·024
B.C.S. "H1"	Mn 0·66	<·03 approx.	0·040
B.C.S. "R"	Mn 0·914, Cu 0·02	None detected by qualitative tests	0·048
B.C.S. "A2"	Mn 0·04, Cr 0·01, Cu 0·067	0·059	0·074
B.C.S. "O1"	Mn 0·617, Cr 0·017, Cu 0·037	0·162	0·153
Stainless steel H Z A	Mn 0·32, Cr 13·5, Si 1·0	0·24	0·22

It will be noted that this table supports the contention that the old methods fail below approximately 0·06 per cent. of nickel.

Notes.

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

THE ACTION OF AIR ON FLOWERS OF SULPHUR AND GROUND SULPHUR.

THE following investigation was carried out to determine the action of air on flowers of sulphur and ground sulphur at various temperatures.

The method employed consisted in passing a known volume of air over the sulphur, which was maintained at a constant temperature, and then passing the air through a standard solution of iodine.

The results obtained are shown in Tables I and II.

TABLE I.

Class of sulphur.	Weight of sulphur taken.	Temperature.	Vol. of air.	*N*/100 iodine.	Equivalent to SO_2 on weight of sulphur taken.
	Grm.		Cb.ft.	c.c.	Per Cent.
Flowers	1	17° C.	1	0·1	0·0032
Flowers	1	25° C.	1	0·2	0·0064
Flowers	1	30° C.	1	0·4	0·0128
Flowers	1	40° C.	1	0·5	0·0160
Flowers	1	50° C.	1	0·7	0·0224
Flowers	1	60° C.	1	0·9	0·0288
Flowers	1	70° C.	1	0·9	0·0288
Flowers	1	80° C.	1	1·1	0·0352
Flowers	1	90° C.	1	1·2	0·0384
Flowers	1	100° C.	1	1·3	0·0416

TABLE II.

Ground	1	17° C.	1	Nil	Nil
Ground	1	60° C.	1	Nil	Nil
Ground	1	70° C.	1	Nil	Nil
Ground	1	80° C.	1	Nil	Nil
Ground	1	90° C.	1	0·2	0·0064
Ground	1	100° C.	1	1·2	0·0384

The apparatus employed to carry out these determinations consisted of first a potash bulb to free the incoming air from any sulphur compounds, followed, in succession, by a drying tube of calcium chloride, a test tube containing the sulphur, a wash-bottle with a known quantity of standard iodine solution, a further wash-bottle with a known quantity of sodium thiosulphate solution, and finally a meter for measuring the volume of air passed over the sulphur.

The introduction of the sodium thiosulphate was found, during the preliminary experiments, to be necessary, as an appreciable quantity of iodine is carried over by the air.

The sulphur in the test tube was covered with a layer of cotton wool to prevent any particles of sulphur passing over in the current of air.

The indicated temperatures were maintained by means of a water-bath, throughout the period of each determination, *viz.* 3½ hrs.

It is apparent from the figures in the above tables that:

(1) Air has little or no action on ground sulphur at temperatures below 90° C.

(2) Appreciable and increasing quantities of sulphur compounds are evolved from flowers of sulphur in the presence of air at temperatures from 17° C. upwards.

The ground sulphur was sufficiently fine to pass through a 100-mesh sieve to the extent of 99·45 per cent. While it is admittedly a comparatively coarse product, this does not explain the apparent inactivity of the ground sulphur at temperatures below 90° C., whilst the flowers of sulphur shows a steady and progressive increase in the amount of sulphur compounds evolved as the temperature rises.

J. E. STEPHENSON.
S. W. BRIDGE.

Notes from the Reports of Public Analysts.

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

CITY AND COUNTY OF BRISTOL.

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1928.

THE total number of samples examined was 1400 (805 formal), of which 87 were adulterated, bringing the adulteration percentage to 6·21 per cent., the highest since 1919. The increase in milk adulteration (72 of 747 samples) was responsible for the high general adulteration rate.

A sample of skim milk was not only adulterated with 16 per cent. of added water, but also contained formaldehyde (0·002 per cent.), which was also present in one sample of milk (0·01 per cent.).

UNFERMENTED CORDIALS.—Eleven samples of unfermented cordials, sold as "non-alcoholic British wine," were examined. These had the following composition:

UNFERMENTED CORDIALS.

Description.	Cider-snap.	Raisin.	Ginger.	Cowslip.	Orange.	Ginger (Brandy).
Sp. Gr.	1041·2	1093·4	1110·0	1112·8	1133·3	—
Alcohol by wt., per cent.	0·68	0·42	0·74	0	0·37	0·10
Alcohol by vol. ,,	0·87	0·53	0·94	0	0·47	0·12
Proof spirit, ,,	1·49	0·93	1·62	0	0·76	0·22
Total solids, ,,	11·27	24·0	26·8	24·4	34·9	48·0
Ash, ,,	0·15	0·026	0·075	0·066	0·050	·14

UNFERMENTED CORDIALS—*continued.*

Description.	Raisin.	Ginger (Brandy).	Ginger.	Raisin.	Orange.
Sp. Gr.	1097·1	—	1102·9	1108·5	1087·5
Alcohol by wt., per cent.	0·54	0	0·39	0·47	0·23
Alcohol by vol. ,,	0·80	0	0·49	0·60	0·29
Proof spirit, ,,	1·39	0	0·86	1·05	0·51
Total solids, ,,	25·92	51·9	26·20	26·26	22·62
Ash, ,,	0·06	0·102	0·095	0·07	0·03

BACTERIOLOGY.—During the year 12,317 specimens were examined.

Examination for Diphtheria.—Westbrook's system of classification was adopted. In this system the Klebs-Löffler and Hoffman organisms are dealt with together as *B. diphtheriæ* of varying forms, beaded, barred and solid types, in degree of virulence in the above order.

The system, however, was modified to this extent, that when slides afforded evidence of complete characterisation, such slides were further specified by the designating letters KL accompanying the old classification; other slides classified as B (a mixed infection) were regarded as suspicious, while those in which Hoffman forms alone occurred were left in Class C.

The following table expresses the results obtained by this modified system, the classes (A and B) KL, B, C representing the presence and extent of the above organisms, with the specimens submitted by the general medical practitioners of that City:

Class (A & B) KL ..	341	10·41	per cent.
Class B	72	2·20	,, ,,
Class C	535	16·34	,, ,,
Negative	2,327	71·05	,, ,,
Total ..	3,275	100·0	,, ,,

There were thus among these, 10·41 per cent. of cases of undoubted diphtheria discovered, and 2·20 per cent. suspicious cases.

Milk.—Of the 122 samples of graded milk examined, 3 of certified milk, 16 of Grade A milk and 5 of Pasteurised Milk did not comply with the Milk (Special Designations) Order, 1923. Of 16 samples of vended milk, 1 was placed in category 1, and 4 in category 2, the remainder falling below the standard of graded milk.

Raisins.—These were alleged to have been damaged by sea-water or sewage. A portion was macerated in sterile water and inoculations made into MacConkey tubes (glucose). No indication of the presence of *B. coli* was obtained, and there was thus no evidence of sewage.

EDWARD RUSSELL.

GIBRALTAR.

REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1928.

THE total number of samples and specimens examined was 4020. There was a marked decline (857) in the number of diphtheria swabs examined, but, apart from this, there was an increase in the other branches of laboratory work. Of the 178 samples of food and drugs examined, 31 (17·4 per cent.) were below the standards set out in the Public Health Ordinance.

GOATS' MILK.—The average composition of the samples of goats' milk was:—Fat, 4·16; non-fatty solids, 9·01 per cent. These figures were well above the statutory limits for Gibraltar, namely, 3·5 per cent. of fat and 8·0 per cent. of solids-not-fat.

GOATS' UNBOILED MILK.—To prevent the introduction of milk-borne diseases from Spain all milk must be boiled before being sold in Gibraltar, and the magistrates deal severely with the offence of selling unboiled milk. Among last year's samples two were found not to have been boiled, and a third sample showed contamination with unboiled milk to the extent of about 5 per cent. In one of these cases a fine of £3 with £1 3s. 0d. costs was imposed.

GOATS' MILK—SKIMMED.—Of the 67 samples of goats' milk examined, no less than 24 were deficient in fat. When samples are taken by the inspectors, it is the general rule for vendors to declare that the milk has been skimmed. By so doing they evade the law, for in a test case brought before the High Courts a few years ago the vendor was successful. Experiments made by me have shown that the fat which rises to the surface of hot milk can easily be worked back into the milk again when cold, and there will then be very little difference, if any, in the fat and non-fatty solid contents. In view of the large increase in this malpractice of skimming in recent years, it was thought desirable that amendments to the existing ordinance should be framed to protect the public (*cf.* ANALYST, 1929, 104).

METALLIC CONTAMINATION OF AERATED WATERS.—A systematic examination of the products of the six aerated water businesses in Gibraltar was made during the latter part of the year. While some were free, or nearly so, from metallic impurities, others contained appreciable and even dangerous amounts of lead (*e.g.* up to 0·5 grain per gallon). The origin of the lead in two of the factories was traced to the use of lead piping to connect the carbonator with the bottle-filling apparatus. In another factory lead was getting into the soda water from the solder on the mixer. These sources of contamination have now been eliminated.

A. G. HOLBOROW.

Legal Notes.

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

SAMPLING AFTER DELIVERY.

ON August 12 a wholesale firm was summoned at Ramsgate for giving a false warranty to a grocery firm in respect of a sale of pepper.

The solicitor for the defence asked that the case should be dismissed on the ground that a copy of the analyst's certificate did not accompany the summons, as is required by the Act, but the Bench decided that the case should proceed.

Evidence was then given that the sample had not been taken in the course of delivery, as provided by the Act, but that delivery took place first.

The Bench upheld the objection and dismissed the summons. The Chairman observed that someone was to blame for not sending the analyst's certificate with the summons, and that the inspector should have been instructed to take the sample before delivery of the pepper was complete.

ARTIFICIAL CREAM: AN APPEAL.

ON September 13, the appeal of a "Pure Milk and Cream Company, Ltd." against convictions at Marlborough Street Police Court (see ANALYST, 1929, 542) was heard at London Sessions.

The Chairman, Sir Robert Wallace, announced that the appeal would be allowed on the ground that the proceedings in the Police Court had not been brought by a body entitled to take proceedings under the Act.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Report No. 33.

A CRITICAL AND HISTORICAL STUDY OF THE PECTIC SUBSTANCES OF PLANTS.*

A STUDY of the chemistry of the pectic compounds shows that *pectose* is not to be regarded as a substance of invariable composition, but a compound of methoxylated pectin in which from 1 to 8 of the methoxy groups may be replaced by cellulose residues; *pectin* is a neutral methoxy ester of pectic acid containing 11·76 per cent. of methyl alcohol; *pectic acid* is a complex galacturonic acid combined with arabinose and galactose, and between pectin and pectic acid are intermediate forms classed together as pectinic acids. The acid extracted with alkali from beets by Scheibler and Votoček and Šebor is a complex arabic acid of the nature of arabin associated with various carbohydrates, glucose, arabinose and galactose, and is not identical with the metapectic acid similarly obtained by Frémy and others from fruits and other plant tissues. Probably metapectic acid is identical with the *d*-galactose-galacturonic acid, $C_{12}H_{20}O_{12}$, described by Ehrlich as a hydrolytic decomposition product of pectin and pectic acid. Both are amorphous, water-soluble, strongly acid, precipitated by alcohol and mineral acids, form water-soluble calcium and barium salts, and, on oxidation with nitric acid, give mucic acid. The confusion as to the decomposition products is largely explained by the fact that galactose and pentose sugars give rise to furfural on distillation with hydrochloric acid.

EXTRACTION OF PECTIC COMPOUNDS.—The various methods for the extraction of the more important pectic compounds from plant tissues are discussed in detail. A new method for extracting pectose by conversion into pectic acid by hydrochloric acid consists in washing with water to remove the bulk of natural acids and soluble pectic substances, and then boiling under a reflux condenser for successive 3-hour periods with $M/75$ hydrochloric acid. The extract is filtered off, the residue washed with water to free it from the soluble pectic material produced, and the boiling repeated until nothing further is extracted (3 to 5 boilings). If boiled for more than 3 hours, the soluble pectic substances produced tend to decompose or alter physically. Aliquot portions of the total extract, including washings, are hydrolysed with soda and precipitated with acetic acid and calcium chloride, and the total pectic content of the tissues thus found. By deducting the amount of soluble pectin obtained in a separate determination by dissolving out with water and alcohol, the pectose present is found.

* By M. H. Branfoot (M. H. Carré). Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. 6d. net.

On ten 50 grm. samples of fresh, uniform, apple tissue the weight of pectose (as calcium pectate) was between 0·73 and 0·77 grms., averaging 0·75 grm. By staining with ruthenium red, pectic substances not affected by the above treatment were still found present in the middle lamella. By boiling the residue after extraction of pectose, pectin, etc., for successive half-hour periods with dilute sodium hydroxide of concentration not exceeding 0·05 per cent., a gradual solution of cellulose was found to take place, and by solution of their middle lamellae the cells become completely separated. The method affords a relative measure of the extent of the occurrence of pectic constituents in the middle lamella.

Quantitative hydrolysis of pectose into pectin depends on a careful adjustment of temperature, time of action and H-ion concentration of the extracting solution. For the preparation of commercial pectin extracts the raw material should be heated for 5 or 6 1-hour periods at 98° C. with approximately 0·1 per cent. nitric acid. Further purification is effected by filtration through kieselguhr.

PURIFICATION OF PECTIN.—Pectin may be purified by a process of electrolysis. A small parchment dialyser containing distilled water is suspended in a bell-jar containing the pectin solution and having a parchment-covered bottom, which is dipped in a large glass trough of distilled water, with a layer of mercury at the bottom to serve as cathode. Tubes for filling and emptying pass through the cork of the bell-jar, and also a tube filled with mercury in the end of which is fixed a platinum electrode of about 2 square cm., to serve as anode; a reverse current causes precipitation of pectin. The current is kept at 0·25 amp., and the heating effect reduced by placing the electrodes as near together as possible. The water in the dialyser should be changed daily. The average ash content of samples of plant material was thus reduced from 3·1 to 0·5 per cent. in 3 days. Pectic acid of a high degree of purity and of a definite chemical composition may be prepared by Schryver and Haynes's method (ANALYST, 1917, **42**, 144).

For the preparation of a clear concentrated and tasteless extract of pectin, on a large scale, Poore's method is satisfactory. The aqueous pectin extract is filtered through kieselguhr, precipitated with 95 per cent. alcohol, and enough absolute alcohol added to the precipitate to convert it into a thick paste. After kneading, the alcohol is removed by pressing. The process is repeated several times at a temperature of 68° C. The purified pectin is then dissolved and concentrated as required.

Pectin may be prepared in powder form by Zoller's method (ANALYST, **1918**, **43**, 270), whereby purification is effected by precipitation and re-solution, centrifuging, dialysis against running water (but electro-dialysis would be preferable), and evaporation *in vacuo* at a temperature not exceeding 40° C., followed by precipitation by alcohol.

DETERMINATION OF PECTIN.—The determination by precipitation of pectic substances as calcium pectate is discussed by Carré and Haynes (*Biochem. J.*, **1922**, **16**, 60), and Carré (ANALYST, 1922, **47**, 263; *Ann. Bot.*, 1925, **39**, 811), and has been found invariably successful by Carré, further confirmation being afforded by Farnell, Hardy and Emmell. The "soluble pectin" of various authors is not necessarily of uniform composition, and the term must be regarded as collective, indicating the mixture of neutral pectin and pectinic acids arising from the various forms of pectose in the tissues.

The relative distribution of the cellulose and pectic material may be ascertained by using Mangin's microchemical methods. By boiling the sections with water for long periods considerable amounts of pectic material are removed from the cell walls, but complete dissociation is not obtained. By boiling with 5 per cent. hydrochloric acid, followed by 2·5 per cent. potassium hydroxide, positive reactions

for cellulose, but negative for pectic compounds are obtained. By treatment with acid alcohol, followed by a solvent for pectic acid such as ammonia, caustic alkali, etc., the pectic compounds modified by the acid are maintained insoluble.

The pectic constituents may be isolated by solution of the cellulose with Schweitzer's reagent.

STAINING METHODS.—Ruthenium red is a valuable stain for the detection of pectic substances if used critically with other stains and combined with chemical methods. The basic stains, such as methylene blue, safranine, etc., do not exhibit specific affinity for pectic substances. Sections are prepared, washed with water, and at once stained in a freshly prepared aqueous solution of ruthenium red (1 part in 5,000 of water). The stain may usually be removed from the non-pectic portions by warming in water. The sections may then be treated on the slide by various reagents effecting decomposition; for example, ammonium oxalate dissolves out all pectic compounds, leaving unaltered cellulose. Hydrochloric acid, followed by potassium hydroxide, may also be used. By such methods the intimate association of the cellulose of the cell walls with pectose was established, and the conception of the middle lamella as a kind of cell cement composed of a complex containing pectic acid or pectates was confirmed.

ENZYMIC DECOMPOSITION.—The distribution of pectic compounds in plant tissues and their possible functions in the plant economy and the changes which the pectic compounds undergo in fruits, especially in the apple, are discussed, together with the enzymes responsible for the pectic changes in certain plant and fruit structures. In the case of pectic decompositions associated with fungal and bacterial diseases a series of pectic changes is effected by enzymes similar to, if not identical with, those normally produced by the plant tissues, and it is probable that the majority of fungal or bacterial secretions contain a mixture of the various enzymes present in normal tissue, *i.e.* pectosase, pectinase and pectase. The secretion of *Rhizopus* (Harter and Weimer), however, probably contained no pectosase. The disintegration of plant tissues produced by fungal diseases, and the similar phenomena accompanying normal death, are regarded as due to a series of pectic changes controlled by enzymes, either present in the living tissues or secreted by the fungi or bacteria.

MANUFACTURE OF FRUIT JELLIES.—In considering the formation of pectin and sugar fruit jellies empirical methods involving concentration by evaporation of unestimated mixtures of the fruit sugar and water are unsatisfactory, because if acid but insufficient pectic materials are present (rhubarb, apricot, strawberry, pineapple, cherry), jelly cannot be produced except by the addition of pectin; or if the fruit contains too little acid (strawberries, cherries, sweet apples, pears, peaches, melons, and figs), prolonged heating merely results in pectic decomposition and caramelisation of the sugar, and acid must be added before jelly is formed (strawberries and cherries are deficient in both pectin and acid). Further, in over-ripe or unsound fruit pectin decomposition has started and increases on heating. A concentration of 0·2 to 1 per cent. of pectin and of acid is regarded as the optimum for jelly production. Pectin is now prepared from many sources, such as sugar-beet residues, and may be added as required. A similar percentage of pectin in different fruits does not necessarily mean similar jellifying powers, and much work has still to be done in this connection. If acid pectin and sugar are present in optimum proportions, 8–10 minutes' rapid boiling produces good jellies. If pectin or acid are deficient, 20 to 30 minutes' boiling will be necessary to bring about concentration by evaporation; but if sugar is deficient, the time will be decreased. More than 30 minutes' boiling is useless, and pectin decomposition takes place, destroying the jellifying power of the mixture. D. G. H.

New South Wales.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1928.

In his final report, Dr. Cooksey, the retiring Government Analyst, states that a record number of samples (20,658) was examined during the year, being an increase of 3000 over the previous year. Of these, 15,945 were milks, 2·5 per cent. of which from the metropolitan area were adulterated, and 4·5 per cent. of those from the country districts.

Food Preservation by Sulphur Dioxide Enabling Act, 1920.—During the year 1928 this Act was added to the list of legal enactments in force in this State. It was passed and put into operation to legalise the Bullot, or similar processes for the preservation of meat. Under Section 4 of the Act, not only meat, but all foods, are allowed to contain sulphur dioxide (or sulphites calculated as sulphur dioxide) in amount not exceeding 3·5 grains per lb. The second paragraph of this Section provides that "sulphur dioxide" must be applied in the form of a gas by a method approved by the Board of Health, but no restriction is placed on the method, or methods, by which sulphites, which are permitted as an alternative preservative, may be added. The omission, however, is one of considerable importance, since it appears that the Section, as worded, is capable of an interpretation obviously not intended by the framers of the Act, and permits the addition of sulphites to foods up to the limit specified. In connection with the approval by the Board of Health of the method by which sulphur dioxide should be applied, an investigation was carried out in the Chemical Laboratory. (*Cf.* p. 601.)

A total of 209 samples of raw meat was examined, 136 of which contravened the requirements of the Regulations of the Pure Food Act by containing a preservative. Of 746 raw sausages examined, 222 contained preservative in excess of the amount permitted, while 11 of 150 cooked sausage meats were adulterated by being deficient in meat and by being artificially coloured. Forty-five samples of tripe were found to contain preservative, 22 of which contained sulphites, 5 formalin, 1 nitrite, and 17 boron compounds.

A special examination was made of a number of tripes prepared by a process requiring the use of sodium perborate. This process produces an article clean and attractive in appearance, possessing good keeping qualities. The chemical examination of the final product offered for sale did not show evidence of the presence of a peroxide, but small amounts of boric acid (in the majority of cases, however, less than one-quarter of a grain per lb.) were present.

Liver Extracts.—Liver extracts having recently been shown to be efficacious in the treatment of pernicious anaemia, a chemical examination of the various commercial preparations on the market was undertaken. Some of these take the form of the dried or desiccated liver substance, whilst others are claimed to be highly active fractions in which the essential principle can be given in concentrated form. The chief disadvantage of the latter type has been its hygroscopic nature, but this is now overcome by packing in sealed glass tubes in dosal quantities.

The composition of the active principle in liver is at present unknown. The analyses, therefore, were not intended as a comparison of the efficacy of the preparations examined, but rather to ascertain as far as possible whether the statements accompanying the articles were correct, and to see that no adulteration was being practised.

Of the two dried liver substances examined, both appeared to be correctly described as having a concentration of four times that of fresh liver, although one sample had considerably more fat than the other.

A good deal of variation in composition, however, is shown in the concentrated fractions ("extracts"), but this may be accounted for by different processes of manufacture. It would appear to be highly desirable to adopt standard methods of manufacture to ensure that liver preparations are of uniform composition, containing the active principle in adequate quantity.

The amounts of copper, iron and zinc were determined in a desiccated substance and in a fractional extract. The other samples analysed were not sufficient in quantity to permit of these determinations being made. From the results obtained in the two samples tested it is inferred that the metallic content bears no relationship to the therapeutic activity.

COMPOSITION OF COMMERCIAL LIVER PREPARATIONS USED IN THE TREATMENT OF PERNICIOUS ANAEMIA.

Sample No.	1.	2.	3.	4.	5.	6.	Average
Country of manufacture	*Australia.*	*England.*	*U.S.A.*	*U.S.A.*	*England.*	*U.S.A.*	composition
Description of sample	Desiccated liver.	Liver extract.	Desiccated liver.	Liver extract.	Liver extract.	Liver extract.	of fresh ox liver.
Weight of substance in container, grms.	114	7·26	28·6	5·88	9·23	2·11	—
Labelled equivalent of fresh liver, grms.	456	226	114	100	226	100	—
Corresponding to:—							
Concentration in comparison with fresh liver	4:1	31:1	4:1	17:1	24·5:1	47:1	—
Water, per cent.	7·80	12·65	7·45	18·60	12·52	9·20	71·2
Ash, ,,	2·97	21·2	5·35	9·95	11·53	9·94	1·6
Phosphoric anhydride ,,	1·58	6·03	2·48	2·62	4·19	5·61	—
Nitrogen, ,,	9·72	7·52	9·63	7·47	2·92	11·16	—
Protein (N × 6·3), ,,	61·2	47·4	60·6	47·0	18·4	70·3	20·4
Fat, ,,	22·7	Nil	8·0	Nil	Nil	Nil	4·5
Carbohydrates (by diff.) ,,	5·33	18·75	18·6	24·45	57·55	10·56	2·3
Metals (*mgrms. per* 100 *grms.*):							
Copper	3·5	—	—	1·8	—	—	—
Iron	22·5	—	—	2·5	—	—	—
Zinc	11·0	—	—	3·1	—	—	—

COD-LIVER OIL TABLETS.—During the year attention was drawn to an American preparation, "Cod-Liver Oil Compound Tablets." Extensive claims in regard to the therapeutic action are made by the manufacturers, cod-liver oil being stated to be "the most active ingredient." It is also claimed that "the extractives used in these tablets contain the entire vitamin content," and "each tablet contains (by extractives) the actual equivalent of a half teaspoonful of cod-liver oil." The chemical test for vitamin *A* indicated that the quantity present in the tablets examined was not more than would be accounted for by the incorporation of a small amount of cod-liver oil in the pill mass, approximately one-quarter of a grain per tablet. That is to say, it would require 225 tablets to yield the equivalent of a medicinal teaspoonful of cod-liver oil. Biological tests were not carried out in this State, but were made in the laboratories of the Pharmaceutical Society, London, and showed the absence of both vitamins *A* and *D*. Stringent regulations are necessary to prevent such gross misrepresentations being made.

TOXICOLOGICAL CASES.—Police and Coroners forwarded exhibits for examination in connection with 68 deaths which formed the subject of inquiry. Among the unusual poisons found in the viscera submitted were arsenate of lead (fruit spray), mercury (a poison which has a very corrosive action on the organs), nicotine, and atropine, the latter derived in the case under notice from liniment of belladonna. In other cases death was found to have been due to strychnine, arsenic, morphine, opium, carbolic acid, formalin (a poison not often used), prussic acid, veronal and cyanide. In 27 cases the analytical examination did not furnish evidence of the presence of poisons. In 4 cases action was taken by the Crown on murder charges, in two of which death was due to slow arsenical poisoning.

In one of these cases, the poison was administered in the form of arsenate of lead (fruit spray), both lead and arsenic being found in the organs.

BLOOD TESTS IN CONNECTION WITH DROWNING.—During the year specimens of blood were forwarded for analysis in connection with deaths supposed to have been due to drowning. It has been found by Gettler (see *U.S. Naval Medical Bulletin*, May, 1922) that in cases of drowning in salt water the blood of the left chamber of the heart contains more sodium chloride than that of the right chamber. In cases of drowning in fresh water the reverse holds, the blood in the left heart containing the lower percentage of sodium chloride. Figures obtained in definite cases of drowning show a difference in the chloride content of the blood of the two chambers of the heart, amounting to at least 19 mgrms. of sodium chloride per 100 grms. of blood.

It is of interest to note that in every case submitted the analytical figures supported the medical diagnosis as to the cause of death, and the method has proved extremely valuable in doubtful cases. The following are the figures obtained in 7 cases examined in the Laboratory:

No.	Sodium chloride. Mgrms. per 100 grms. of blood.		Conclusions drawn from chemical examination.
	Left heart.	Right heart.	
1	566	494	Salt-water drowning.
2	603	603	Death not due to drowning.
*3	424	450	Fresh-water drowning (see note below).
4	440	441	Death not due to drowning.
5	547	466	Salt-water drowning.
6	612	512	Salt-water drowning.
7	540	492	Salt-water drowning.

The following is a brief description of the method of determination used.† A definite weight or volume of the blood is suitably diluted, and the protein precipitated by a solution of picric acid. The precipitate is removed by filtration, and to an aliquot portion of the filtrate is added a definite volume of silver nitrate solution of known strength. After shaking, the precipitate is allowed to settle, and the liquid filtered. The excess of silver nitrate is determined in a portion of the filtrate by means of standard potassium iodide solution.

* In the case of No. 3 carbon monoxide was also present in the blood to the extent of 50 per cent. saturation. The man, while working in a sewer, was overcome by an escape of gas, and fell unconscious into a comparatively small amount of water.

† For fuller details see "Determination of the Chloride Content of the Blood of the Heart in cases of Death by Drowning," by Gettler, *U.S.A. Naval Medical Bulletin*, May, 1922.

BENZENE POISONING.—In one case in which death was due to asphyxiation by benzene (benzol) fumes, no chemical alteration was detected in the blood, but an unusual feature was noted, namely, that the blood did not clot on keeping.

CARBON MONOXIDE POISONING.—In two cases in which death was due to gas poisoning carbon monoxide was present in the blood to the extent of 50 per cent. saturation. A case of interest to the motoring public was that in which a man was found dead sitting at the wheel of his car, which was in the garage with the engine still running. Death was found to be due to poisoning by carbon monoxide, one of the products of incomplete combustion.

Union of South Africa.

FOOD, DRUGS, AND DISINFECTANTS ACT.*

AN Act (No. 13 of 1929), which is to come into force on a date to be fixed by proclamation, is intended to "consolidate and amend the laws for regulating the labelling, and preventing the importation or sale of food and drugs which are unwholesome or adulterated, or incorrectly or falsely described, and for regulating the labelling and preventing the importation or sale of disinfectants which are incorrectly or falsely described" in the Union of South Africa.

Article 4 of the Act enumerates the conditions under which food or drugs will be regarded as adulterated or falsely described.

Articles 6 and 7 prohibit the sale of food or drugs adulterated or falsely described, or not up to the standard demanded by the purchaser, or which have been subjected to injurious abstractions, admixtures or processes.

Article 8 prohibits the importation, manufacture, or sale of any food advertised or described as specially suitable for the use of invalids or infants, which contains any preservative other than sugar or common salt.

Article 10 deals with the responsibility of the importer, manufacturer or packer of food or drugs sold in sealed original packages; and Article 11 with the inspection, sampling, analysis, and detention of imported products.

Articles 13 to 18 give special provisions relating to the sale, description, etc., of flour, meal, bread, coffee, honey, milk, and milk products.

Disinfectants imported or sold must bear a label stating (*a*) the name and address of the manufacturer and, when sold, of the seller; (*b*) full directions for use, including the proportion, strength or dilution in which it is effective; and (*c*) the names of its active ingredients or proportion of each, or in the case of a liquid germicide, its germicidal power or efficacy, expressed in numerical terms as compared with a standard, and as ascertained by a method prescribed by regulation (Art. 19).

The Minister is empowered to apply the provisions of the Act to any ointment, cream, powder or similar substance for use on the human skin or hair, to soap, tobacco, cigars, cigarettes, snuff, chewing gum, and any other substance.

The Minister may also make regulations prescribing the nature and composition of food and drugs, and, in general, for carrying into effect the purposes of the Act.

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* From *Board of Trade J.*, 1929, p. 592. The text of the Act, which is, in the main, identical with the Bills introduced in 1927 and 1928, may be seen on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

Sulphur Dioxide in Meat.

INVESTIGATION OF THE BULLOT PROCESS FOR THE PRESERVATION OF MEAT.*

FOR the purpose of the investigation, the treatment of the meat intended for examination was carried out in an enclosed space having an approximate dimension of 20 ft. in length, 8 ft. in width and 7 ft. in height. Under normal working conditions, this would be sufficient for the treatment of 150 carcases of sheep. The carcases of one sheep, one pig, a half-side of beef, and sausages and small goods (heart, liver, kidney, etc.) were treated. The powder used in the generation of the gases was found to be of the following composition:—Saltpetre, 11; sulphur, 22; charcoal and bark, 67 per cent.; with a small quantity of essential oil.

It was particularly noticeable that where muscular tissue was exposed to the fumes, discoloration was evident to depths varying to one-half inch. Where, however, the tissue was protected with a layer of fat and skin, the penetration of the sulphur dioxide depended on the thickness of the protecting layer, as did also the discoloration (if any). The leg of pork, for instance, which was covered with a layer of fat and skin one-half inch thick, showed only very slight discoloration. It will be seen by a comparison of the results of analysis of the mutton and pork in Table I that the penetration of the sulphur dioxide is dependent on the thickness of the covering layer of skin and fat. The leg of mutton, which was covered with a thin skin only, contained 7·1 grains of sulphur dioxide per lb., while the leg of pork, protected by a half-inch layer of skin and fat, contained only 3 grains per lb. The small goods (liver, kidney, heart, etc.) which have comparatively large surfaces without a protecting skin, absorbed large quantities of sulphur dioxide (see analyses given in Table I).

Samples of treated and untreated mutton and pork were suspended under similar conditions, at room temperature, for the week 8th to 14th August inclusive). The maximum temperature during this time was 76·8° F., and the minimum temperature 47·4° F., the average mean daily temperature being 58·1° F. The treated mutton and pork appeared to be in good condition at the end of this period, but the untreated meat showed distinct signs of decomposition.

The treated beef did not keep well. As, however, it was delivered to the Laboratory in sections, the test as to its keeping qualities could not be carried out under normal conditions, since (presumably) the whole carcase is usually allowed to hang uncut until it is required for use.

Three analytical tables are appended, Table I showing the amounts of sulphur dioxide present in samples cut from different portions of the carcases, Table II showing the loss of sulphur dioxide on keeping uncooked meat, and Table III showing the amount of sulphur dioxide lost in cooking.

* Appendix to the Annual Report of the Government Analyst for New South Wales, for the year 1928.

TABLE I.

Sulphur Dioxide Content of Meats Treated by the Bullot Process.

Date of treatment.	Date of analysis.	Kind of meat.	Portion tested taken from	Amount taken for analysis. Grms.	Sulphur dioxide. Grains per lb.	Remarks.
7.8.28	8.8.28	Roast beef, 1st cut	*Average sample	100	10·4	Bleached where exposed to gas.
,,	9.8.28	,, ,, 2nd ,,	Outside meat	,,	8·0	Colour normal, except where exposed to gas (small portion only).
,,	,,	,, ,, ,, ,,	About 1 in. in	,,	0·3	
,,	,,	,, ,, ,, ,,	*Average sample	,,	2·0	Sample approximately 2½ in. thick.
,,	,,	,, ,, ,, ,,	Average fat	,,	0·9	
,,	,,	Thick flank of beef	Outside meat	,,	3·5	Colour normal, except small portion exposed to gas.
,,	,,	,, ,, ,, ,,	About 2 in. in	,,	less than 0·1	
,,	,,	,, ,, ,, ,,	*Average sample	,,	1·0	
,,	,,	Bone (beef)	*Average sample	,,	0·15	
,,	8.8.28	Leg of mutton	*Average sample	,,	7·1	Bleached where exposed to gas.
,,	9.8.28	Leg of pork	*Average sample	,,	3·0	Bleached where exposed to gas.
Untreated	8.8.28	Sausages (not treated by Bullot process)	*Average sample	,,	2·0	Sausages as ordinarily sold, containing SO_2 within prescribed limits, and *similar to those used in experiment.*
7.8.28	,,	Sausages (similar to above and treated by Bullot process)	*Average sample	,,	24·2	Bleached where exposed to gas.
,,	,,	Sheep's liver, etc.	*Average sample	,,	24·1	Bleached on outside.
,,	,,	Pig's liver, etc.	*Average sample	,,	25·2	Bleached on outside.
,,	,,	Bullock's heart	*Average sample	,,	8·9	Bleached on outside.

* Average sample is a portion taken right through sample so as to represent, as nearly as possible, the whole.

TABLE II.

Loss of Sulphur Dioxide on Keeping Uncooked Meat.

Date of treatment.	Kind of meat.	Amount taken for analysis. Grms.	Date of analysis.	Sulphur dioxide. Grains per lb.	Sulphur dioxide lost in 2 days. Grains per lb.	Sulphur dioxide lost in 6 days. Grains per lb.	Sulphur dioxide lost in 7 days. Grains per lb.
7.8.28	Leg of mutton	100	8.8.28	7·1	—	—	—
			10.8.28	3·6	3·5	—	—
			15.8.28	1·1	—	—	6·0
,,	Leg of pork	,,	9.8.28	3·0	—	—	—
			15.8.28	0·9	—	2·1	—
,,	Pig's liver, etc.	,,	8.8.28	25·2	—	—	—
			10.8.28	14·2	11·0	—	—
,,	Sausages (treated)	,,	8.8.28	24·2	—	—	—
			10.8.28	23·4	0·8	—	—

The mutton and pork were exposed to the air; the pig's liver and sausages were kept loosely wrapped in paper.

TABLE III.

Sulphur Dioxide in Meat Lost in Cooking.

Date of treatment.	Date of analysis.	Kind of meat.	Amount taken for analysis. Grms.	Weight. Before cooking. Grms.	Weight. After cooking. Grms.	Sulphur dioxide. Grains per lb. Uncooked meat.	Sulphur dioxide. Grains per lb. Cooked meat.	Remarks.
7.8.28	10.8.28	Leg of mutton	100 uncooked 76 cooked	140	76	3·6	2·5	Cooked by gentle boiling for 1 hour with approx. 4 parts of water.
,,	15.8.28	,,	100 uncooked 100 cooked	—	—	1·1	0·6	Baked. Weight 2–3 lb.
,,	10.8.28	Sausages (treated)	100 uncooked 90 cooked	141	95	23·4	20·2	Cooked by frying for 20 minutes; when cooked had acid taste and odour of SO_2.
,,	10.8.28	Pig's liver, etc.	100 uncooked 94 cooked	138	94	14·2	6·5	Cooked by gentle boiling 1 hour with approx. 4 parts of water.

Taking into consideration the loss in weight in cooking, the actual amount of sulphur dioxide lost represents two-thirds of the total in boiling and one-third in frying.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Modification of the Fiehe Test for the Detection of Artificial Invert Sugar in Honey. E. K. Nelson. (*J. Assoc. Off. Agric. Chem.*, 1929, **12**, 323–324.)—A solution of 2 grms. of sample in 10 c.c. of water is extracted rapidly with ether in a Palkin and Watkin's apparatus for 30 minutes, the extract concentrated to 5 c.c., 2 c.c. of a fresh 1 per cent. solution of resorcinol in concentrated hydrochloric acid added, and the mixture immediately shaken. After 5 minutes pure honey gave a very faint pink, whilst in the presence of 10 to 20 per cent. of invert sugar a deep pink to dark red colour was obtained. Re-extraction of the residues showed that all the oxymethyl furfural had been removed. J. G.

Detection of Fruit Wine in Grape Wine. B. Bleyer and W. Diemair. (*Chem. Ztg.*, 1929, **53**, 621, 641–642.)—The following modification of Werder's method (ANALYST, 1929, 422, 476) is reliable for the detection of 10 per cent. of fruit wine in grape wine:—The wine (100 c.c.) is shaken with 7 grms. of pure animal charcoal for 20 minutes, heated, filtered hot and evaporated under reduced pressure

in Werder's apparatus (*loc. cit.*). When 5 c.c. remain, the hot liquid is centrifuged to remove any deposit of tartar, and evaporated further to a syrup (1·2 to 1·5 grms.). This is shaken for 1 hour with 0·2 c.c. of benzaldehyde and 1 c.c. of sulphuric acid (1:1), and the crystals allowed to separate over-night. Dibenzal mannitol forms fine needles, whereas dibenzal sorbitol is an amorphous gelatinous mass. The corresponding triform acetals are needle-shaped crystals, m.pt. 227° and 206° C., respectively; they are prepared from a solution of the precipitate by the action of equal weights of formalin and concentrated hydrochloric acid heated under a reflux condenser for 1½ hours. J. G.

Determination of Carotin in Flour. C. G. Ferrari and C. H. Bailey. (*Cereal Chem.*, 1929, **6**, 347–371.)—The authors criticise the tentative method of the A.O.A.C. on the grounds of its inability to yield consistent results, owing to the presence of invisible suspended matter in the filtered petroleum spirit solution of carotin. By increasing the efficiency of filtration with paper pulp or unglazed porcelain low results are obtained, since a portion of the carotin is adsorbed by the filtering media. The following modification is claimed to yield reliable results, although approximately 20 per cent. of the carotin is retained by the flour, the remainder only being actually determined:—Twenty grms. of the sample are weighed into a glass-stoppered bottle, and 100 c.c. of petroleum spirit are added from a pipette. After agitation at frequent intervals the mixture is allowed to stand in a dark place over-night, and the supernatant liquid is siphoned off and filtered in the following manner. An alundum thimble is fitted by means of a rubber ring into a glass adapter, the stem of which is passed through a rubber stopper in the lid of a vacuum desiccator containing a little petroleum spirit to saturate the atmosphere. The thimble is rinsed several times with small portions of the carotin solution, each portion being drawn through under a slight vacuum. A graduated cylinder is then placed under the adapter, and 50 c.c. of the carotin solution are filtered slowly, the thimble being filled to a depth not exceeding 5–6 mm. The transmittancy of a 10 cm. depth of the solution is then determined in a spectrophotometer using a wave-length of 4358 Å. derived from a mercury vapour lamp, and is compared with that of a petroleum spirit solution of pure carotin. Experiments have shown that corresponding results are obtained if the petroleum spirit is replaced by "gasolene," the latter having the advantages of lower volatility and lower price. The use of filtering media may be avoided in the determination by the following method, which, however, occupies a longer time. After agitation as described in the previous method the mixture is allowed to stand in darkness for 48 hours, and the supernatant liquid is slowly separated by means of a capillary syphon. Details are given of the precautions necessary in transmittancy measurements, the effect of altering the ratio of weight of sample and the volume of solvent, and the influence of various milling products, such as bran and shorts, upon the results. Tables showing the results obtained with different varieties of Canadian wheat and various products obtained in milling are given. (*Cf.* ANALYST, 1927, **52**, 446.) T. J. W.

Separation of Solid Fats into their Constituents. A. Van Raalte. (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 1058–1060.)—Lund's work (*Z. Unters. Nahr. Genusm.*, 1922, **44**, 113) on the relation of the proportions of fatty acids in a fat to the sp. gr., refractive index, iodine, saponification and acetyl values is criticised in that it provides no means of distinguishing between fats containing the same fatty acids attached to different hydroxyl groups of the glycerol molecule. A method is proposed for solid fats in which the crystalline portion of the fat is removed from the amorphous portion by shaking 10 grms. of the solid fat with 10 c.c. of 96 per cent. alcohol and sufficient acetone (20 to 30 c.c.) to coagulate the crystals. The amorphous fat dissolves at ordinary temperatures, and may be removed by filtration, the crystals being washed twice with 20 c.c. of a mixture of equal volumes of alcohol and acetone, the filtrate evaporated, and the residue dried and weighed. Mutton tallow, beef fat, horse fat, and lard, yielded 4·8, 3·6, 5·4, and 6·6 grms. of liquid phase, respectively, the refractive indices (40° C.), aniline points (temperature of separation of a mixture with aniline), and iodine values of which were shown to be considerably higher, lower and higher, respectively, than those of the corresponding solid phases. J. G.

American Reindeer Fat. W. F. Baughman, G. S. Jamieson and R. S. McKinney. (*Oil and Fat Ind.*, 1929, **6**, 11–12.)—The analysis of five samples of reindeer fat taken from different parts of two carcases gave the following figures:—M. pt., 45·8–48·6° C.; sp. gr. at 40°/25° C., 0·8981–0·8993; $n_D^{60°}$, 1·4510; saponification value, 194·3–199·2; iodine value (Hanus), 33·7–39·4; acetyl value, 5·0–8·0; Reichert–Meissl value, 0·0–0·3; Polenske value, 0·3–0·5; unsaponifiable matter, 0·4 per cent.; acid value, 2·0–8·6; saturated acids, 53·6–59·9 per cent.; unsaturated acids, 41·4 per cent. (of iodine value, 90·0). The composition of the fat was: Oleic acid, 36·8; myristic, 6·7; palmitic, 35·0; stearic, 20·5; and arachidic acid, 0·7 per cent. D. G. H.

Fatty Oil of the "Pilgrim" Whale (*Cetorhinus Maximus*, Günner). Biological Relations between the Cholesterols and Squalene. E. André and H. Canal. (*Bull. Soc. Chim.*, 1929, **45–46**, 498–511.)—The oil of a young male specimen of this whale (sp. gr. 15/0° C. 0·9105, n_D^{20} 1·4865, $[\alpha]_D$ — 6° 54′, saponification value 98·7, Hanus iodine value 155·2, acidity 0, acetyl value 0) represents only 6 per cent. of its weight, whereas the yield from an adult is 12·5 per cent. (*id.*, 1927, **41**, 921). After saponification it yielded 40·5, 58·5 and 3·21 per cent. of unsaponifiable matter, fatty acids and glycerol, respectively. The first was divided into two portions by alternate treatment with acetone and petroleum spirit. One was crystalline and was shown, by m.pt. and iodine value determinations of the products obtained by fractional crystallisation from petroleum spirit, to contain 3 parts of ordinary cholesterol, $C_{27}H_{46}O$, and one of a cholesterol having two ethylenic linkages (iodine value 133·0). It represented 22·5 per cent. of the weight of the oil, and is the largest quantity of cholesterol obtained from any animal oil or fat. The other (liquid) portion was fractionally distilled and found

to consist of 1 part of pristane, $C_{18}H_{38}$ (Tsujimoto, *Ann. de Chim.*, 1927, **7**, 69) and 4 parts of squalene. Bromination experiments with the latter confirmed the authors' opinion (*loc. cit.*) that the addition of hydrogen bromide gas does not proceed to completion, and experiments with iodine bromide indicate the formula $C_{27}H_{44}$ for squalene. Separation of the fatty acids by Tsujimoto's method (*loc. cit.*), and by fractional crystallisation of the lead and lithium salts, led to the identification of 15 per cent. of arachidonic acid, myristic acid (20 per cent.), cetoleic acid (55 per cent.), and therapeutic acid, $C_{18}H_{28}O_2$ (10 per cent.), of which 32 per cent. was in the form of glycerides, while the remainder was combined as esters and cholesterols. The transformation—fatty acids—⩾cholesterols—⩾squalene—indicated by these figures corresponds with the increase in maturity of the animal and suggests a close chemical and physiological relationship between squalene and cholesterol (*cf.* following abstract). Further, the presence of a high proportion of hydrocarbon mixed with alcohols having a high optical rotation supports the theory of the marine origin of petroleum. J. G.

Marine Animal Oils. Oil of *Centrophorus Granulosus*. E. André and H. Canal. (*Bull. Soc. Chim.*, 1929, **45–46**, 511–524.)—The methods outlined in the preceding abstract were applied to the unsaponifiable matter of the oils extracted from the eggs, of foetus oil, and of the fat of adult animals. The eggs yielded 29·6 per cent. of a brown oil containing 43·5 per cent. of fatty acids with high molecular weight and iodine value, 4·7 per cent. of a mixture of at least two cholesterol alcohols of which one had two ethylenic linkages (*cf. loc. cit.*), 50·4 per cent. of a mixture of highly unsaturated hydrocarbons (squalene), and 3·9 per cent. of glycerol. A similar oil appeared in the foetus fat, except that the fatty acids and cholesterol alcohols were less, and the hydrocarbons greater in quantity. The fats of growing and adult animals yielded unsaponifiable matters rising progressively to 91 per cent. in the latter case, and were composed principally of highly unsaturated hydrocarbons derived from the glycerides of the fatty acids of the clupanodonic series, the cholesterol alcohols being intermediate products (*cf. loc. cit.*). This transformation of clupanodonic glycerides into cholesterols and then into hydrocarbons may be followed progressively from the composition of the oils from the egg and foetus and of the fats of the young and adult animals. J. G.

Thiocyanogen Value of Strophanthus Oil and of Oils of the Chaulmoogra Group. E. I. Van Italie. (*Pharm. Weekblad*, 1929, **66**, 677–683.)—Kaufmann's determination of the thiocyanogen value (*T*) (ANALYST, 1928, **53**, 613) has been applied to the oil extracted by petroleum spirit from *Kombé strophanthus* (sp. gr. 0·9270; n_D^{25}, 1·4701; acid value, 19·0; saponification value, 193·5, Wijs iodine value *I*, 95·1, *T* 67·4). The percentages of linolic, oleic and saturated acids were then calculated from the accepted values of *R* and *T* for linolic and oleic acids by means of the expressions 1·104 (*I*–*T*), 1·112 (2*T*–*I*) and by difference, respectively (*cf.* Matthes and Rath, *Arch. Pharm.*, 1914, 683), and found to be 30·5, 44·3 and 25·2 per cent., respectively.

For samples of chaulmoogra and hydnocarpus oils the values *I* 100·6 and 95·7 and *R* 99·1 and 94·8 were found, respectively (*cf.* Hashimoto, ANALYST, 1925, **50**, 566; Bömer and Engel, *id.*, 1929, 423). The presence in chaulmoogric acid, $C_{18}H_{32}O_2$, of an asymmetric carbon atom attached to an unsaturated cyclic residue was also confirmed.

Gorli-oil, obtained from the African tree *Oncoba echinata* (André and Jouatte, ANALYST, 1928, **53**, 604) contained 10 to 12 per cent. of the highly unsaturated acid $C_{18}H_{30}O_2$, and had m.pt. 40° C., n_D^{40} 1·4722, [α] 49·02, *I* 93·4, acid value 5·6, saponification value 200·4, *T* 93·2. J. G.

Composition of Wool Fat. J. C. Drummond and L. C. Baker. (*J. Soc. Chem. Ind.*, 1929, **48**, 232–238T.)—Crude merino wool was extracted with light petroleum, yielding crude fat which contained only small quantities of free fatty acids or alcohols and consisted largely of the fatty acid esters of the higher aliphatic alcohols, and of cholesterol and isocholesterol. No glycerol was present and only negligible traces of nitrogen or phosphorus-containing fatty substances. The fatty acids consisted almost entirely of the saturated acids, cerotic, palmitic and stearic, and no evidence of high oxygen acids was obtained. The unsaponifiable matter consisted of cholesterol, isocholesterol and higher aliphatic alcohols. Isocholesterol was separated from cholesterol by removing the latter with digitonin, and no other method was found satisfactory. It had a m.pt. of 139–140° C. and $[\alpha]_D$ +84°. The colour reactions resemble those of certain sterols. The compound is unsaturated, but the degree of unsaturation is not yet established. It is not readily reduced by hydrogen in presence of palladium, and more work is required to establish the formula. The name isocholesterol is misleading, and lanosterol is suggested. Ergosterol was not found in the unsaponifiable matter. D. G. H.

Rapid Method for Quinine Determination. G. A. Sticht. (*Chemist Analyst*, 1929, **18**, [iii], 6–7.)—In the case of cinchona bark 66·667 grms. of 40-mesh powder are shaken continuously for 2 hours, or intermittently for 6 hours, with 50 c.c. of 20 per cent. ammonia and 501 c.c. of a mixture of 105 c.c. of chloroform and 420 c.c. of toluene at 20° C., and 250 c.c. filtered through cotton wool. The filtrate is then shaken thoroughly, but not violently, with 25, 20 and 20 c.c. successive portions of 15 per cent. sulphuric acid, the combined extracts evaporated at a low temperature to 50 c.c., gently boiled, and ammonia added until the solution is slightly alkaline to methyl orange. A solution of 6 grms. of citric acid in 10 c.c. of water is made slightly alkaline to phenolphthalein with sodium hydroxide solution, boiled and added to the hot extract, and the acid quinine citrate, which separates on cooling, is filtered off in a Gooch crucible, washed with 70 c.c. of water, dried at 100° C., and weighed. The factor $3 \times 0{\cdot}6279$ gives the percentage of anhydrous quinine, and the herepathite test may be used to confirm the purity of the precipitate. Other alkaloids may be determined in the wash-liquors. J. G.

Identification of Atropine by means of Wagner's Reagent. C. C. Fulton. (*J. Assoc. Off. Agric. Chem.*, 1929, **12**, 312–317.)—Wagner's test gives the following types of atropine crystals increasing in size in the order given according as 2·75, 8, 35 and 50 grms. of potassium iodide, respectively, are used in the presence of 1 grm. of iodine and 100 c.c. of water:—(1) Small red-brown rods, (2) small yellow plates, (3) a mixture of yellow and dark red crystals, (4) orange-red, hexagonal, elongated plates with dark-red diamond-shaped or triangular grains and a few yellow cubes. The corresponding optimum ranges of concentration of the test solution are 1:5,000 to 1:50,000, 1:800 to 1:5,000, 1:650 to 1:2,000, and 1:200–1:800, respectively, but the first reagent has been found to give a positive reaction with a 1:200,000 solution of atropine. Hyoscyamine was found to give similar crystals, and one sample of atropine gave crystals of abnormal shape. J. G.

Assay of Jalap. L. E. Warren. (*J. Assoc. Off. Agric. Chem.*, 1929, **12**, 324–332.)—Comparative trials of six methods led to the rejection of the U.S. Pharmacopoeia X and Jenkins' methods on account of the high results obtained, and of other methods involving the use of aliquot portions. Dale's method was found accurate but tedious, and the following is recommended:—The drug is ground to a No. 60 powder, and 10 grms. extracted with 50 c.c. of alcohol for 30 minutes under a reflux condenser, and then percolated with warm alcohol till 100 c.c. of tincture are obtained. Of this, 25 c.c. are evaporated and extracted for 2 minutes with 15 c.c. portions of boiling water until no more colour is removed. The residue, after filtration, is extracted thoroughly with warm alcohol, the extract evaporated, and the resin dried to constant weight at 100° C. J. G.

Keeping Properties of Digitalis and some of its Preparations. H. B. Haag and R. A. Hatcher. (*Amer. J. Pharm.*, 1929, **10–11**, 474–480.)—There is no evidence that ground digitalis leaf deteriorates during a period of many years if kept with reasonable care. Fluid extracts and tinctures of digitalis decompose but slowly, and at somewhat variable rates, and infusions at a slightly more rapid rate, but the latter may be used with confidence for several weeks. No toxic substances develop during deterioration, and dosage may be increased to correspond with the degree of deterioration. Probably a substance causing decomposition of some active principles is present in digitalis, itself being decomposed in the process, and there is also a substance resisting deterioration. Very old tinctures have nearly 70 per cent. of the activity of average fresh tincture of good quality. Acidity is not the chief factor in decomposition, nor is a low alcohol percentage the sole cause. Ampoules should be made of a glass containing a minimum amount of soluble alkali. D. G. H.

Determination of Nitrate Nitrogen in Tobacco. H. B. Vickery and G. W. Pucher. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 121–123.)—Two portions of 5 grms. of the powdered tobacco are placed in separate flasks, 30 c.c. of water and 5 c.c. of 50 per cent. sodium hydroxide solution are added to each, and the mixtures are submitted to steam distillation, 800 c.c. of distillate being collected

in receivers containing hydrochloric acid. These distillates may be used for the determination of the nicotine by the silicotungstic acid method. The contents of the flasks are then diluted to 25 c.c., 15 c.c. of sulphuric acid (1:1) are added to each, and to one flask 3 grms. of reduced iron are added. The mixtures are boiled for five minutes, diluted to 200 c.c., treated with 35 c.c. of 50 per cent. sodium hydroxide solution, and distilled. The difference between the amounts of ammonia found in these distillates is a measure of the nitrate nitrogen in the tobacco. The control determination described above cannot be avoided, since a small quantity of ammonia is always formed when the sample is heated with sulphuric acid. W. P. S.

Quantitative Analysis of Certain Medicinal Preparations containing Mercury. A. Jonesco-Matiu and A. Popesco. (*Ann. Chim. analyt.*, 1929, **11**, 225–231.)—The method depends upon the titration of the mercury ion by the chlorine ion after transformation into mercuric sulphate and precipitation by sodium nitroprusside, and is now extended to the determination of calomel, corrosive sublimate, mercuric ammonium chloride, mercury ointments, mercuric iodide, grey ointment, and iodide ointments. For example, 1 grm. of corrosive sublimate is dissolved in 80 c.c. of water, made up to 100 c.c., and the mercuric oxide precipitated from a known volume with 40 per cent. sodium hydroxide, the solution centrifuged, and the precipitate washed, dissolved in concentrated sulphuric acid, transferred to 80 c.c. of water, 12 drops of sodium nitroprusside solution added, and then 0·1 *N* sodium chloride solution, until the cloudiness disappears. In the case of ointments 10 c.c. of sulphonitric oxidising mixture are added, and the organic matter destroyed, after which crystals of mercuric sulphate are deposited; or the fat may be dissolved in ether and the mercury collected by centrifuging.
D. G. H.

Biochemical.

Storage of Manganese and Copper in the Animal Body and its Influence on Haemoglobin Building. R. W. Titus and J. S. Hughes. (*J. Biol. Chem.*, 1929, **83**, 463–467.)—The fact that young rats from mothers fed on a whole wheat-milk powder diet became anaemic much more rapidly than young rats from mothers on a more complex ration suggested to the authors the probability of a prenatal supply or storage of the haemoglobin-building elements. Titus, Cave and Hughes (*J. Biol. Chem.*, 1928, **80**, 565) showed that manganese, as well as copper, is effective in the utilisation of iron in haemoglobin building. Data presented now show that both manganese and copper are apparently stored in the animal body when these mineral supplements are added to the ration, and that manganese, as well as copper, when given as food or stored in the animal body, is effective in the utilisation of iron in haemoglobin building. Young rats fed on milk supplemented with manganese chloride, and others fed on milk supplemented with copper sulphate, showed a gradual decrease in the haemoglobin content of their blood until the time the manganese or copper supplement was discontinued. On the addition then of an

iron supplement the haemoglobin content of the blood began to increase until it became almost normal. A third lot of rats on milk supplemented with iron for the entire experimental period gradually became anaemic, but not so quickly as when no iron was added as a supplement. It is possible, therefore, that the animal is able to utilise a small amount of iron, owing, not to copper or manganese as an impurity in the food, but rather to a prenatal storage of these elements in the body. The experimental data are shown in graphic form. P. H. P.

Excretion of Lead in Urine. H. Millet. (*J. Biol. Chem.*, 1929, **83**, 265–268.)—Recent work by various workers on the excretion of lead has shown that the major part of the excretion is found in the faeces, and that healthy men, many of whom have had no definite exposure to lead, excrete lead normally in urine and faeces. An investigation has now been carried out which deals with the determination of the total lead excreted in the urine of (*a*) a few healthy persons, (*b*) a number of cancer patients who had received intravenous injections of colloidal lead phosphate, and (*c*) cancer patients resident in the same nursing home, who had not been treated with lead. Lead was determined electrometrically as lead ion by the use of a fluid lead amalgam electrode, operated in the absence of oxygen, as recently described by Millet (*Tr. Faraday Soc.*, 1929, **25**, 147). The electrometric method is accurate to about 2 per cent., but, owing to the risk of contamination with lead in the treatment of the urine, the accuracy of the determinations may be lessened. The treatment of the urine was based on the work of Fairhall (*J. Biol. Chem.*, 1924, **60**, 485; ANALYST, 1924, **49**, 490), who found that ammonia precipitates practically all the lead from urine. The tabulated results show that there is a definite normal excretion of lead in urine. In cancer patients who had received the injections of a lead phosphate colloid, and in cancer patients not treated with lead, the excretion was about the same, and averaged about 0·085 mgrm. of lead per litre. The average figure found is the same as that recorded for healthy persons by Kehoe, Edgar, Thamann and Sanders (*J. Amer. Med. Assoc.*, 1926, **87**, 2081), whose method was less accurate. There is no evidence that the lead injected was at any time being excreted in the urine. Single doses of the lead phosphate colloid contained usually 50 mgrms. of lead, and thus an increase above the normal level of excretion would be expected to appear if the lead injected was being excreted through the kidney. It may be mentioned that lead phosphate, which is very insoluble, produces practically no toxic symptoms, and damages the kidney very little. P. H. P.

A Previously Undetected Constituent of Blood. E. W. Rockwood, R. G. Turner and J. J. Pfiffner. (*J. Biol. Chem.*, 1929, **83**, 289–297.)—A previously undetected substance, which reduces arsenophosphotungstic acid, is shown to be present after acid hydrolysis of the blood of man, dog and rabbit. It is also found in the muscle, kidney and liver of dog and rabbit. In the few ox and pig bloods examined it was detected only in traces. This substance has provisionally been named substance Z. A method is described for its determination in tungstic acid blood and tissue filtrates, and its amounts have been determined in

normal and various pathological bloods. In protein-free tungstic acid blood filtrates, uric acid, thioneine and substance Z are present, and all give the same blue colour with alkaline arsenophosphotungstate. Acid hydrolysis of the protein-free filtrate liberates uric acid, and it is now shown by the authors that acid treatment of the thioneine fraction increases the material measured by the arsenophosphotungstate reaction, and thus produces substance Z. Therefore to determine the quantities of uric acid, thioneine and substance Z in blood, oxalated blood was used, and four colorimetric determinations were made on each sample: (1) uric acid direct, (2) uric acid indirect, (3) thioneine plus substance Z, and (4) thioneine. A part of the blood filtrate was hydrolysed with sulphuric acid, a part was not so treated; uric acid, both direct and indirect, was determined in the unhydrolysed portion. Substance Z is freed by acid hydrolysis and is then precipitated by silver lactate, but is not afterwards liberated by acid sodium chloride solution. Therefore it was determined with thioneine in the silver residue from the hydrolysed portion. Thioneine was similarly determined in the unhydrolysed portion, and the amount of substance Z was found by subtraction. All tissue filtrates were prepared from the warm organs according to the method of Folin, Berglund and Derick (*J. Biol. Chem.*, 1924, **60**, 361). In a discussion it is shown that substance Z is not the same as any of the known constituents of tungstic acid blood and tissue filtrates.

P. H. P.

Quantitative Changes in the Chloroplast Pigments in the Peel of Bananas during Ripening. H. von Loesecke. (*J. Amer. Chem. Soc.*, 1929, **51**, 2439–2443.)—An investigation was undertaken to gain some knowledge of the changes which the pigments in banana peel undergo when the fruit is ripening (changing from green to yellow), and of the cause of the yellow colour. The three pigments, chlorophyll ($a+b$), xanthophylls and carotin were determined. Other pigments are present, as during the separation process there were indications of flavones and anthocyanins, but these latter are present in the cell sap, whilst chlorophyll, xanthophylls and carotin are present only in the specialised portions of the protoplasm known as plastids. The fruit was peeled, the pulp side of the peel scraped free from pulp, and the peel then cut into small pieces and ground in a mortar with sand. It was extracted in the cold with 30 per cent. aqueous acetone to remove gums and flavones. The chloroplast pigments were then extracted with pure acetone after the method of Schertz (*Plant Physiology*, 1928, **3**, 211). The extracted chlorophylls were saponified to chlorophyllins, and determined colorimetrically with a solution of chlorophyllins prepared from pure chlorophylls as a standard. Xanthophylls and carotin, after extraction and separation from the chlorophylls, were determined colorimetrically with the use of a solution of naphthol yellow as a standard for the former, and naphthol yellow and orange G as a standard for the latter, after the method of Sprague (*Science*, 1928, **67**, 167). The comparisons with these dyes could not be made by artificial light. The percentages of total sugar (as invert) were determined on the pulp of the fruit from which the peel was taken. This is the best criterion of the ripeness of the fruit. From the data obtained the following conclusions have been reached:—The

chlorophyll content of the peel ranges from 102·9 to 51·7 mgrms. per kilo. of fresh peel in the unripe fruit at discharge from the boat, and decreases as the fruit ripens. Chlorophylls decrease as a straight line function of time. The total yellow pigments (xanthophyll plus carotin) remain approximately constant throughout the maturation of the fruit; therefore the yellow colour of an unripe banana is masked by chlorophyll. The amount of xanthophylls is always greater than the amount of carotin, the range of the former being from about 5 to 7 mgrms. per kilo. of fresh peel, whilst the range of the latter is from 1·5 to 3·5 mgrms. per kilo. of fresh peel. P. H. P.

Antimony Trichloride Colour Test for Vitamin *A*. N. Evers. (*Quarterly J. Pharm.*, 1929, **2**, 227–237.)—In normal cases the author recommends the addition of 2 c.c. of reagent, made from recrystallised antimony trichloride and less than a month old, to 0·2 c.c. of a mixture of 2 c.c. of oil and 8 c.c. of dry chloroform. The colour is read in the tintometer in a 1 cm. cell exactly 30 seconds after the addition of the last drop of reagent, and 85 times the number of blue units gives the units of vitamin *A* per grm., corresponding approximately with the U.S.P. biological unit. If necessary, the quantity of oil used should be altered so as to obtain a colour of between 4 and 6 blue units, and the factor adjusted accordingly. The quantity of sample taken is of particular importance with highly active fats such as ox liver fat, 0·0005 mgrm. of which gave a distinct colour, but any error involved when small quantities of sample are used may be minimised by the addition of sufficient inactive oil (*e.g.* arachis oil or ox liver fat irradiated so as to destroy the vitamin) to bring the total oil concentration to 2 per cent. The natural colour of ox liver fat appears to modify the relation of the colours obtained from two different quantities of the fat. J. G.

Comparison of Biological and Colorimetric Assays for Vitamin *A* as Applied to Fish Oils. E. R. Norris and I. S. Danielson. (*J. Biol. Chem.*, 1929, **83**, 469–475.)—All evidence so far published seems to indicate that the colour produced with arsenic trichloride, or with the chloroform solution of antimony trichloride, with oils, is associated with the vitamin *A* content of the oil tested, but no exact data are available to show a quantitative relationship between the colour produced by either of the above reagents and feeding experiments on the oils. The colour reaction of a series of six fish body and fish liver oils with antimony trichloride has now been studied, and an attempt made to correlate the colour with careful feeding experiments which had been made on each oil. The solution of antimony trichloride in chloroform was cooled to the temperature of ice-water (2 to 4° C.), and allowed to remain until equilibrium was reached, when a clear solution was obtained which contained about 18 per cent. (weight/volume per cent.) of antimony trichloride; this permitted the use of lower temperatures than room temperature under ordinary laboratory conditions, for a long enough period to obtain an accurate reading. A series of dilutions of cod-liver oils, ratfish liver oil, chinook, sockeye, silver, and humpback salmon body oils, was prepared in chloroform. To measure each dilution 0·3 c.c. of it was placed in

a cell in a Lovibond tintometer, 3 c.c. of the cooled reagent added (mixing being accomplished by delivering the reagent in a strong stream into the cell), and the colour produced after 10 to 15 seconds matched with standard Lovibond units; a reading was taken at the end of 30 seconds. Figures show the results obtained when the intensity of the colour produced is plotted against the mgrms. of oil used in the reaction. It is definitely concluded that the blue colour produced by a fish oil and antimony trichloride reagent is not proportional to the amount of oil used; therefore it is not directly proportional to the vitamin *A* content, if the colour reaction is produced by this factor. At no concentration is the curve obtained with varying amounts of cod-liver oil in antimony trichloride reagent linear. However, the curves approach a straight line at very low colour values, so that, by plotting the lower values on a larger scale, the amount of each oil required to give the same colour as that obtained with 0·00099 grm. of cod-liver oil (1 animal unit which=2·18 Lovibond blue units) may be read on the abscissa. These values, given to the nearest 10 mgrms., are shown to agree fairly well with those obtained biologically. Therefore the colorimetric assay upon the fish oils tested agrees within reasonable limits with the biological assay when the technique described is used. P. H. P.

Improvements in the Method of Isolating the Anti-Beri-Beri Vitamin. B. C. P. Jansen. (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 984–985.)—By replacing the phosphotungstic acid by silicotungstic acid and the alcoholic solution of platinum chloride by a solution of cadmium chloride in the original method (Jansen and Donath, *Medeleel. Dienst Volksgezondreid Nederlandsch-Indië*, 1927) the yield of anti-beri-beri vitamin from rice bran may be doubled. D. G. H.

Bacteriological.

Rapid and Accurate Method for Determination of the Quantity of Yeast or other Micro-Organisms in a Suspension. R. J. Williams, E. D. McAlister and R. R. Roehm. (*J. Biol. Chem.*, 1929, **83**, 315–320.)—Recent methods described for the determination of yeast crops have all been tried, but none has been found highly satisfactory; their disadvantages are outlined. The authors have devised a new method which can be used not only to determine yeast crops, but also to standardise very dilute suspensions for seeding. This method involves the interposing of the yeast suspension in a suitable cell between a 6 to 8 voltage light and a specially prepared thermo-couple, and determination of the E.M.F. set up by the thermo-couple. An inexpensive galvanometer is sufficiently sensitive to allow an accurate determination of the amount of yeast in suspension. A weighed quantity of starch-free baker's yeast (69·5 per cent. moisture) was suspended in 0·08 *M* sugar solution, and 14 different dilutions were prepared from the original. Each of the suspensions was interposed (with the same cell) and the galvanometer deflections recorded. By changing slightly the resistance in series with the lamp to compensate for the slow drop in the battery voltage, a constant deflection was maintained when a cell of distilled water was interposed. The

galvanometer showed very little "zero creep" after the thermo-couple had been illuminated for a short time. The curve obtained (yeast in suspension: galvanometer deflections in cm.) is shown. Unknown samples, prepared by one author and tested by another, gave very good results. Details are given of the apparatus required, its arrangement, and the preparation of the thermo-couple. That used in this work consists of a receiver of foil (tin or platinum, blackened on the side exposed to the radiation), and two small wires, one of bismuth and the other an alloy of bismuth and tin (95·5 per cent. Bi, 4·5 per cent. Sn by weight). These are "spot welded" together, and to the centre of the receiver in one operation, and their other ends are welded (or soldered) to two relatively heavy copper leads. The junctions of the two wires with the receiver is the hot-junction of the thermo-couple, and their junctions with the copper leads constitute the cold junction. The couple should be inclosed in an air-tight container of glass. This new method is rapid, accurate, and can be used over a very wide range of concentrations. Apart from its use with yeast, the apparatus can be used to determine the quantities of bacteria or other organisms in suspension (possibly quantitatively suspended matter of various kinds), and hence should be a very useful tool in the field of biochemistry. P. H. P.

Organic Analysis.

Use of Aldehydes and Di-hydroxy Acetone in the Detection and Differentiation of Phenols. A. H. Ware. (*Quarterly J. Pharm.*, 1929, **2**, 249–253, 254–264, 265–266.)—(1) The phenol (0·05 grm.) is dissolved in 3 c.c. of concentrated sulphuric acid, 1 drop of 10 per cent. oxantin (di-hydroxy acetone) solution added, and any colour-change noted. Five per cent. hydrobromic acid is then added, a drop at a time, until the maximum colour change is reached, and finally water is added in the same way and any further change noted. (2) A crystal of tartaric acid, smaller than a pinhead, is gently warmed with a solution of 0·05 grm. of the phenol in the concentrated acid until fumes appear, and the colour noted. (3) To obtain the greatest amount of differentiation, 2·5 c.c. of a mixture of 1 c.c. of formalin and 99 c.c. of concentrated sulphuric acid are mixed with 2·5 c.c. of a sulphuric acid solution of the phenol (0·01 to 0·05 grm.). Water is added, drop by drop, the mixture shaken, and the colour-change noted. If a dark precipitate is obtained, it is best to add the mixture slowly to 6 c.c. of alcohol. The three following tests are more suited to mixtures of phenols with other substances. (4) An extract of the sample (free from alcohol and resin) in 10 c.c. of 0·5 to 7·5 *N* hydrochloric acid, diluted if possible till almost colourless, is precipitated with 5 drops of formalin at the boiling-point, cooled, re-heated and cooled, and the precipitate filtered off from the hot solution. The precipitation or otherwise of a particular phenol, the rate of reaction, the colour of the precipitate, and its solubility in alcohol or 5 per cent. aqueous alkali depend on the nature of the phenol, the strength of acid, the time and the temperature, and qualitative separations and differentiation tests for phenols based on these lines are tabulated. (5) Di-hydroxy acetone may replace formalin in acid solutions not weaker than 7·5 *N*,

but this reagent is less suitable for separation purposes. A better colour is often obtained by the addition of a few drops of hydrogen peroxide at the moment the colour change appears. (6) Stain tests may be carried out with a deal shaving dipped in the solution, dried, dipped in hydrochloric acid and gently warmed. Or a solution of 0·01 grm. of phenol in 1 c.c. of alcohol, with 1 drop of formalin or dihydroxy-acetone solution is allowed to fall on 2 filter papers, one above the other, on a warm tile, and 5 drops of strong hydrochloric acid added while the papers are still slightly moist. The colour changes are noted when the papers are almost dry, again after addition of 1 drop of hydrogen peroxide and 2 more drops of acid, and finally after addition of ammonia. The results of each test are summarised for a number of phenols. Cresol in carbolic acid is detected by the gradual admixture in the cold of 5 drops of phenol solution with a mixture of 2 drops of a 2 per cent. alcoholic solution of vanillin and 5 c.c. of hydrochloric acid. A rose-pink colour is given by 1·5 per cent. or more of ortho- or meta-cresol, or both, within 3 minutes. If the mixture is then poured into potassium hydroxide solution, the colour will be intensified if ortho-cresol is present (*cf.* ANALYST, 1927, **52**, 335). J. G.

Determination of Phenols. J. A. Shaw. (*Ind. Eng. Chem., Anal. Edit.*, 1929, **1**, 118–121.)—A special method of steam-distillation is described, the phenols being determined subsequently by means of the turbidity produced by the addition of bromine. Ten c.c. of the sample, which may contain up to 0·1 per cent. of phenols, are placed in a test-tube and acidified with a few drops of dilute sulphuric acid. The test tube is closed with a cork and connected by suitable tubes with a condenser and a second test-tube containing water. Both test-tubes are placed in a steam chamber and heated at 100° C. A current of air is then blown through the tubes, passing first through the test-tube containing water, then through the test tube containing the sample, and thence to the condenser. When 25 c.c. of distillate have been collected, small portions of it are diluted successively until the concentration of the phenol is reduced to about 35 parts per million. A portion of the diluted distillate is then treated with bromine water, and the turbidity produced compared with those obtained by treating known amounts of phenol with bromine. These standards may conveniently contain from 30 to 35 parts of phenol per million, and the comparisons should be made at 20° C. Alcohols, amines, aldehydes, organic bases, oils and inorganic salts interfere and must be removed before the phenol is determined. W. P. S.

Identification of Primary Phenylethyl Alcohol in Essential Oils and Mixtures of Perfumes. S. Sabetay. (*Ann. Chim. Analyt.*, 1929, **11**, 193–195.)—The fraction corresponding to phenylethyl alcohol is slowly distilled with coarsely powdered potassium hydroxide and the fraction coming over at 140–160° C. collected. This consists of styrolene (recognised by its smell) if phenylethyl alcohol was originally present. Its presence is confirmed by forming the dibromo derivative, which melts at 72° C. The accidental presence of geraniol or rhodinol does not interfere unless they are present in great excess. The reaction

is particularly useful in perfumery practice in dealing with synthetic alcohols of closely approximating b.pts., and the quantity of dibromostyrolene formed affords a rough indication of the proportion of phenylethyl alcohol originally present.

D. G. H.

Cresyl Esters of Phenyl-Acetic Acid. L. C. Raiford and J. G. Hildebrand. (*Amer. J. Pharm.*, 1929, **101**, 481–484.)—The *p*-cresyl ester of phenylacetic acid is included as a synthetic perfumery compound in the list of the U.S.A. Tariff Commission, but few data as to its properties are available. The isomeric cresyl esters of phenylacetic acid may be prepared by the action of phenyl acetyl chloride on the cresols. The chloride is made by heating 1 part of phenyl acetic acid and 1·5 to 2 parts of thionyl chloride for 3 hours at 80–100° C. in a flask fitted with a thermometer and with a connecting tube high enough (40 cm.) to prevent thionyl chloride passing over, and with another thermometer at its bend. The excess of thionyl chloride is distilled off under atmospheric pressure, and the residue fractionated under reduced pressure. At 100–101° C. with 16 mm. pressure 92 per cent. of phenylacetyl chloride was obtained as a colourless heavy liquid. Sixteen grms. of the chloride mixed with 11 grms. of freshly distilled *para*-cresol, heated at 90° C. until evolution of hydrochloric acid ceases, cooled, and poured into 200 c.c. of chilled 6 *N* sodium hydroxide solution yielded 83 per cent. of solid *p*-cresyl phenyl acetate in small blocks of m.pt. 74–75° C. This differs from the m.pt. given by Poucher, *viz.* 86° C. (*Perfumes, Cosmetics and Soaps*, Vol. I, p. 97). The *meta* salt was obtained as colourless plates with a yield of 72 per cent., and had a m.pt. of 51–52° C. and the *ortho* salt (yield 82 per cent. of colourless plates) had a m.pt. of 44–45° C.

D. G. H.

Volumetric Determination of Sulphur in Crude Petroleum. G. Woodward. (*Ind. Eng. Chem., Anal. Edit.*, 1929, **1**, 117–118.)—A quantity of the petroleum, sufficient to produce from 0·03 to 0·25 grm. of sulphuric acid, is burned in an oxygen bomb, the contents of which are then dissolved in a small quantity of water, 0·2 c.c. of concentrated potassium iodide solution is added, and any yellow colour due to the liberation of iodine by ferric salts is destroyed by heating the solution after adding a small quantity of aluminium powder. After cooling, alcohol is added in amount sufficient to make the alcoholic strength of the solution 50 to 70 per cent., and the sulphuric acid is titrated with standardised lead nitrate solution. The end-point of the titration is sharp, since in a 50 to 70 per cent. alcoholic solution yellow lead iodide does not form until all lead sulphate has been precipitated.

W. P. S.

Electrostatic Method for the Determination of Fusain in Bituminous Coal. J. D. Davis and J. A. Younkins. (*Ind. Eng. Chem., Anal. Edit.*, 1929, **1**, 165–167.)—The coal is ground to pass a 60-mesh sieve, and 0·5 grm. of the sample is submitted to centrifugal action with a mixture of light petroleum and carbon tetrachloride (sp. gr. 1·40–1·45). This treatment floats most of the coal, which is removed, and the mass of fusain, etc., at the bottom of the centrifuge tube is trans-

ferred to a watch-glass and dried. The dried residue is then spread on the bottom plate of an electrostatic separator. This consists of a glass case; the bottom electrode is an aluminium tray, and the top electrode is a sheet of lead foil glued to the glass. The whole case is mounted so that it may be shaken automatically and slowly. When a high tension current is passed between the electrodes the fusain is attracted and repelled alternately; the motion of the particles is rapid, and if a current of dry inert gas is passed through the case, the fusain may be removed from the field and collected. The coal and foreign substances remain on the bottom electrode. The separated fusain should be examined microscopically to ascertain whether a further treatment is necessary to remove any adhering coal particles.

W. P. S.

Inorganic Analysis.

Quantitative Determination of Neon in Natural Gases. N. P. Péntcheff. (*Compt. rend.*, 1929, **189**, 322–324.)—Argon, krypton and xenon are adsorbed on coconut charcoal at the temperature of liquid air from the mixture of rare gases (obtained after removal of the common gases by the usual methods), and their absence confirmed by spectral analysis. The density of the residual helium-neon mixture is then determined. The method was tested on mixtures in known proportions of the above rare gases, and the results obtained for a natural gas from a Bulgarian spring were shown to confirm Moureu and Lepape's astrophysical theory.

J. G.

New Method for the Separation of Lead and Bismuth. Frick and Engemann. (*Chem. Zeit.*, 1929, **53**, 601–602.)—The method is suitable for the determination of bismuth in metallic lead, and obviates the previous precipitation of lead as sulphate. The nitrate solution (300 c.c.) is treated with 3 to 5 drops of Congo red solution (1·5 per cent.), the blue flocculent precipitate of the dye assisting in the subsequent precipitation. Neutralisation to a blue-red tint is effected with sodium hydroxide. The solution is stirred and treated with 0·7 per cent. cinchonine hydrochloride solution. The precipitate is filtered off after half an hour; a few drops of filtrate are tested with potassium iodide solution for complete precipitation of bismuth (traces of bismuth suffice to impart a brown tint to the lead iodide precipitate). If bismuth is indicated, the neutralisation has not been pushed far enough, and the filtrate must be re-treated after suitable addition of alkali. The precipitate is washed free from lead with cold water containing 10 c.c. of cinchonine solution per litre and neutralised to blue-red by addition of a little Congo red and dilute nitric acid. Filter and precipitate are boiled with 100 c.c. of water and 20 c.c. of nitric acid. The pulped paper is removed by filtration, the filtrate evaporated with 20 c.c. of sulphuric acid until white fumes are freely given off, and the bismuth determined by the usual colorimetric iodide method. The precipitation by the cinchonine salt appears to be a hydrolytic one. Accurate results are claimed.

W. R. S.

Rapid Determination of Mercury and Cadmium. G. Spacu and G. Suciu. (*Z. anal. Chem.*, 1929, **77**, 334–343.)—*Mercury.* The neutral or faintly ammoniacal solution (80 to 500 c.c.) is treated with an excess of potassium iodide and, near the boiling-point, with a boiling concentrated solution of copper diethylenediamine nitrate, $Cu[C_2H_4(NH_2)_2]_2(NO_3)_2.2H_2O$ in excess. On cooling, tabular deep blue-violet crystals separate. They are collected on a porous porcelain crucible, washed with a solution containing 0·1 per cent. each of potassium iodide and of the precipitant, with alcohol, and finally with ether, and weighed after 5 to 10 minutes' drying *in vacuo*. The precipitate has the composition $(HgI_4)Cu[C_2H_4(NH_2)_2]_2$, and contains 22·49 per cent. Hg. The method is applicable in presence of ammonium chloride and nitrate; hence an *aqua regia* solution can be submitted to the process after neutralisation with ammonia. The reagent may be prepared by treatment of a copper sulphate solution with one of ethylenediamine until the characteristic deep blue colour is produced; an excess of the base is not harmful. *Cadmium.*—The neutral solution containing an excess of potassium iodide is boiled and treated exactly as described under Mercury, except that the precipitate is washed with a solution containing one per cent. of potassium iodide and 0·3 of the precipitant, followed by alcohol and ether. The precipitate has the same constitution as the mercury compound and contains 13·99 per cent. Cd. The precipitant must not, in this case, contain free ethylenediamine, nor should ammonium salts be present. The determination is stated to be less advantageous than that of mercury. W. R. S.

Determination of Small Quantities of Copper with 5, 7-Dibromo-*o*-Oxyquinoline. L. W. Haase. (*Z. anal. Chem.*, 1929, **78**, 113–124.)—The method is designed for the rapid determination of copper (0·5 to 10 mgrms. per litre) in industrial water, sewage, etc. A 0·5 per cent. solution of the base in 5 *N* hydrochloric acid is used. Two hundred c.c. of the sample are treated in the cold with a moderate excess of the reagent, and the precipitate coagulated by 20 minutes' digestion on the water-bath. The precipitate is dried at 105° C. for an hour, then heated for 2 to 3 hours at 150° C. for the volatilisation of the excess of precipitant, and weighed. The acidity of the liquid to be tested should not exceed 0·2 *N*; at 0·5 *N* concentration, the small quantity of copper fails to precipitate. Alkaline waters are acidified (methyl orange). Acetic acid and alkali salts do not interfere. Organic colloids, humic acid, etc., in sewage are first destroyed by treatment of the water with one c.c. of *N* hydrochloric acid and 10 drops of perhydrol, and gentle boiling till the liquid is colourless. Any precipitate thus produced is filtered off, previous to the precipitation of the copper. W. R. S.

Accuracy of the Gutzeit Method for Arsenic. J. R. Neller. (*J. Assoc. Off. Agric. Chem.*, 1929, **12**, 332–341.)—A study has been made of the accuracy of the method for aliquot portions of lead arsenate solutions obtained by dipping sprayed apples in 10 per cent. hydrochloric acid. The average probable percentage error of the mean of all the possible pairs obtainable in a number of groups of 8 to 11 determinations each was 6·6 per cent., and this represents the normal

limit of accuracy of the method. The results were independent of temperature between 18° and 33° C., and were the same whether the stannous chloride was added before or after the solution was heated with potassium iodide. In the presence of sulphuric acid, however, the stannous chloride should be added when the solution is finally cooled, so as to avoid formation of sulphur dioxide. Hydrochloric acid is preferable to sulphuric acid, which may produce hydrogen sulphide, and the reduction of arsenate to arsenite should be carried out in 10 per cent. acid solution at 80° C. for 10 minutes. J. G.

Preparation of Antimony-Free Arsenious Oxide and Determination of Minute Amounts of Antimony in Arsenious Oxide. C. W. Foulk and P. G. Horton. (*J. Amer. Chem. Soc.*, 1929, **51**, 2416–2419.)—In the preparation of arsenious oxide of a high degree of purity, antimonious oxide is by far the most troublesome of the impurities to remove. A rapid and simple method for the preparation of antimony-free arsenious oxide is now described, and also an application of this method to the qualitative detection and rough quantitative determination of minute amounts of antimony in arsenious oxide. Briefly stated, the new method consists in the conversion of the arsenious oxide into arsenious chloride, by distillation of the oxide in concentrated hydrochloric acid in a current of hydrogen chloride gas; this is then followed by removal of the antimony by repeated shaking out of the chloride in a separating funnel with concentrated hydrochloric-acid. The antimonous chloride is so much more soluble in concentrated hydrochloric acid than is arsenious chloride that shaking out with only a few portions of acid will completely remove a considerable amount of it. The lower layer is drawn off and the process repeated until the acid layer shows no antimony *vide infra*. Hydrolysis of the arsenious chloride to give arsenious oxide again is accomplished by allowing the chloride to run slowly from a separating funnel into a large beaker of boiling water with vigorous stirring. On cooling, arsenious oxide separates as a fine white solid which is filtered, washed free from acid, and further purified by recrystallisation and sublimation. The acid layer is tested for antimony as follows:—The layer is heated in the distillation apparatus as long as any oily arsenious chloride which it holds in solution distils over. The residue is then transferred to a beaker and treated, while still hot, with hydrogen sulphide. All the arsenic remaining is precipitated as yellow arsenious sulphide, antimony being left in solution. The precipitate is filtered off on a double filter paper, and the filtrate diluted with three times its volume of water, and again saturated with hydrogen sulphide, when antimony, if present, comes down as orange antimonious sulphide. To detect very minute amounts of antimony, the solution should be left to stand for a day or two, for an orange-coloured turbidity may become a distinct precipitate. Less than 0·001 per cent. can be detected by this test. Fairly good quantitative determinations can be made by comparing the precipitated sulphide with a series of similarly prepared precipitates of known amounts of antimony. If only a trace of antimony is suspected in the case of arsenious oxide, the residual acid solution in the distillation flask, after separation of the arsenious chloride, is examined for antimony. P. H. P.

Permanganate Titration of Antimony in White Metal. A. Wassilieff and H. Stutzer. (*Z. anal. Chem.*, 1929, **78**, 97–102.)—When sulphuric acid is used for the solution of the sample and the acid diluted with water and hydrochloric acid previous to permanganate titration, a small amount of antimony is adsorbed by the lead sulphate, and escapes titration. The following procedure is recommended: 1 grm. is boiled with 15 c.c. of strong sulphuric acid until sulphur dioxide is completely expelled. After cooling, 50 c.c. of water, 10 c.c. of strong hydrochloric acid, and again 150 c.c. of water are added. The solution is titrated at 15° C. with 0·1 *N* permanganate till the pink end-point persists for one minute during agitation. The flask is inclined to allow the precipitate to settle; the liquid is cautiously decanted, and the precipitate dissolved by warming with 20 c.c. of hydrochloric acid and 10 of water. The solution obtained is transferred to a 500 c.c. flask, diluted with 400 c.c. of water, and the titration concluded at 15° C. In a series of tests, 1·56 to 3·34 per cent. of the antimony content was found in the lead sulphate. W. R. S.

Colorimetric Method for the Micro Analysis of Cobalt. L. Michaelis and S. Yamaguchi. (*J. Biol. Chem.*, 1929, **83**, 367–373.)—It is ascertained by a colorimetric method that the oxidised cobalt complex of cysteine contains cobalt and cysteine in the ratio of 1:3. This fact in combination with the amount of oxygen necessary to obtain this complex from its constituents suggests as formula for the oxidised cobalt complex of cysteine: $Co(SCH_2.NH_2CH.COO)_3H_2$. A sensitive and accurate method is described for the micro analysis of cobalt which is based on the formation of this complex. The procedure is as follows:—The cobalt compound to be analysed, in such an amount as to contain no more than 5 mgrms. of cobalt, is heated in a platinum crucible with about 1·5 c.c. of concentrated sulphuric acid. The platinum crucible is placed in a larger nickel crucible and heated to dryness. After cooling, 25 c.c. of phosphate buffer (Sörensen) P_H 7·5 and cysteine hydrochloride crystals in excess (*i.e.* about 10 mgrms.) are added, and the oxidation of the cobalt complex is accomplished by the gentle shaking of this solution in a beaker so as to expose it to the air. Oxidation is complete in a minute or so, and the brown colour is stable over many hours or longer. It is then compared in a colorimeter with a solution freshly prepared in the same way from a known amount of cobalt sulphate ($CoSO_4+7H_2O$ crystals free from nickel and iron), which need not be heated with sulphuric acid. Analyses of known amounts of cobalt in range from a fraction of 1 mgrm. up to 5 mgrms. were correct within at least ± 5 per cent. The volume of the solutions may be smaller, if necessary, and $\frac{1}{40}$ mgrm. of cobalt can be determined with the same accuracy. The presence of iron, copper or manganese does not interfere with this method. Nickel can just be detected by a slight change of colour when the ratio of cobalt:nickel=1:2; it is not likely to be present in so large an excess in tissues. The fact that, in general, the removal of nickel is unnecessary imparts a considerable advantage to this method compared with the method applied by Bertrand and Macheboeuf. P. H. P.

Determination of Chromium Oxide (CrO_3) in Lead Paints. E. J. Davis. (*Chemist Analyst*, 1929, **18**, [iii], 8.)—The oxide is extracted from 1 grm. of the vehicle-free pigment in 50 c.c. of a boiling 16 per cent. solution of potassium hydroxide, the diluted solution filtered, and the residue well washed. The extract (400 c.c.) is neutralised at 60° C. with glacial acetic acid, and 15 c.c. added in excess to precipitate lead chromate, while lead sulphate is retained in solution. After 30 minutes the former is filtered off in a Gooch crucible, washed, dried and weighed. In the presence of zinc chromate 2 grms. of lead chloride are added before the addition of the acetic acid. Prussian blue and other pigments do not interfere, and an accuracy of $\pm 0{\cdot}1$ per cent. is obtainable. J. G.

Volumetric Determination of Sulphur in Polysulphides. P. Szeberényi. (*Z. anal. Chem.*, 1929, **78**, 36–40.)—The polysulphide solution is boiled with a known excess of 0·1 *N* sodium sulphite solution: the conversion to thiosulphate is complete after 2 to 3 minutes, the liquor becoming colourless. After cooling, the solution is titrated with 0·1 *N* iodine. The conversion of polysulphide into monosulphide does not bring about any change in the iodine consumption; that of sulphite into thiosulphate, on the other hand, reduces the iodine consumption to one-half. Another portion of liquor is titrated direct with 0·1 *N* iodine: this volume is added to that equivalent to the 0·1 *N* sulphite solution, and the iodine consumption of the sulphite-treated portion subtracted from the above sum. The difference, multiplied by 0·0032, gives the quantity of polysulphide sulphur proper (*i.e.* sulphur in excess of monosulphide sulphur). The thiosulphate invariably present in polysulphide liquors does not affect the accuracy of the determination. W. R. S.

Analysis of Insecticides containing Fluorine Compounds. L. Hart. (*Ind. Eng. Chem., Anal. Edit.*, 1929, **1**, 133–135.)—*Mixtures of alkali silicofluorides and boric acid.*—The silicofluoride is precipitated as its potassium salt in the presence of alcohol (1:2), and, without removing the precipitate, the boric acid remaining in solution is titrated in the usual way. The total acidity is titrated in another portion of the sample, and the difference between this and the acidity due to boric acid is a measure of the alkali silicofluoride. One c.c. of 0·2 *N* sodium hydroxide solution is equivalent to 0·0094 grm. of sodium silicofluoride. *Preparations containing soluble fluorides and arsenic compounds.*—The arsenic is oxidised by hydrogen peroxide and precipitated as silver arsenate from acetic acid solution in the presence of sodium acetate. After filtration the arsenic and fluorine may be determined in the precipitate and filtrate, respectively, by the usual methods. *Mixtures of sodium fluoride, sodium bifluoride and sodium silicofluoride.*—The total acidity of the sample, due to bifluoride and silicofluoride, is determined, phenolphthalein being used as indicator; the titration should be carried out in a platinum vessel and while the solution is boiling. The neutral solution is diluted to 200 c.c., and an aliquot portion used for the determination of total fluorine. To determine the bifluoride, 0·5 grm. of the sample is treated in a platinum basin with 1 grm. of potassium chloride, 25 c.c. of water and 25 c.c. of alcohol.

The mixture is cooled to 0° C., and kept at this temperature while the acidity due to bifluoride is titrated. The difference between this titration and the total acidity gives the amount of the silicofluoride. The fluorine equivalent of bifluoride and silicofluoride deducted from the total fluorine gives the quantity of fluorine present as fluoride. W. P. S.

Physical Methods, Apparatus, etc.

Photo-Chemical Methods of Testing Sources of Ultra-Violet Radiation. **F. C. Hymas.** (*Quarterly J. Pharm.*, 1929, **2**, 281–291.)—In McKenzie and King's method (*Practical Ultra-Violet Therapy*) 2 c.c. of carbon tetrachloride are exposed for 10 minutes in a quartz tube at a distance of 17·5 cm. from the source of radiation, and the chlorine (liberated according to the equation $2CCl_4=C_2Cl_6+Cl_2$) is determined by titration with sodium thiosulphate in the presence of potassium iodide. Since the reaction occurs principally in the vapour phase, the method is not recommended, as the test is susceptible to temperature variations, and the reagent and reaction products cannot be accurately transferred to and from the tube. Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, **47**, 718) expose, under the same conditions, 2 c.c. of a solution containing 6·3 grms. of oxalic acid and 4·27 grms. of uranyl sulphate per litre and titrate the products of catalytic decomposition of the former (carbon dioxide and formic acid) with 0·02 *N* potassium permanganate solution in the presence of sulphuric acid. The present authors measure in terms of the Lovibond scale the blue colour produced from a 0·1 *N* solution of potassium iodide containing 0·1 per cent. of dissolved starch. It is shown that the last two methods give accurate results for the first 20 minutes of exposure, the temperature coefficients per 10° C. being 1·035 (between 25° and 45° C.) and 1·042 (between 25° and 62° C.), respectively. Discrepancies in comparative results are due to the fact that a layer 2·5 cm. thick of the oxalic acid and uranyl salt solution effects complete extinction below 3600 Å. and partial absorption to 4100 Å., whilst potassium iodide and starch solution absorbs all rays below 2625 Å. completely, and partially to 3500 Å. The author's method showed that the emission from 6 lamps fell rapidly during the first 1000 hours of use to a low constant value, corresponding, presumably, with the absorption band of the decomposed silica. J. G.

Reviews.

INDUSTRIAL CARBON. By C. L. MANTELL, Ph.D. Pp. x+410. With 89 Text Figures. New York: D. Van Nostrand Company, Inc.; London: Chapman & Hall. 1929. Price 21s. net.

This is one of a number of Industrial Chemical Monographs which have been planned under the joint editorship of Drs. W. Lee Lewis and Harrison E. Howe. The present one deals solely with carbon and its industrial applications, and the

appearance of the book affords evidence not only of the importance of carbon in the many and diverse forms in which it finds application in industry, but also of the increasing specialisation which is such a striking feature of present-day chemical industry. There was need for a book of this character, if only for the purpose of bringing within one volume the increasing amount of information relating to carbon and its uses—information hitherto found widely scattered amongst the pages of many scientific papers, technical journals and patent specifications. It is to be questioned, however, whether the present volume is sufficiently abreast of the times and as critical as might be wished for one to be able to accord its author unstinted praise.

On the first page one reads: "Due to its dirty habits and uncultured nature, carbon has often been in the step-child's position; as a result of its black, grimy outward appearance and its shy habits but very little attention has been paid to it in the literature." This is the language of the films; other passages in similar vein in the earlier pages are indicative of the somewhat popular manner in which the book is written. One is disposed to disagree with the view that "but very little attention has been paid to it in the literature." In the reviewer's opinion, a great deal of information respecting carbon has found its entry into technical literature in recent years, and it is charitable to assume that, owing to the author's "shy habits," he has failed to notice or appreciate some of this, for otherwise the omissions are difficult to understand.

There are twenty-nine chapters in the present volume, many of them very short and containing but a few pages in all. The subject-matter embraces the study of graphite (both natural and artificial), carbon black and other black pigments, charcoal considered as a fuel, the various decolorising and adsorbent charcoals, carbon electrodes, carbons for arc-lights and other special purposes, battery and welding carbons, and carbon refractories. The treatment embraces, in addition, the applications of these various materials in the arts and manufactures. Throughout the book there are copious references to original scientific and technical publications and research and patent specifications, mainly of United States origin. But there are a number of important omissions in this respect, and, as few of the references bear a later date than 1923, the present volume is not as up-to-date as the reader has a right to expect.

The chapters dealing with graphite are quite good and leave nothing to be desired. In regard to carbon black too little notice has been accorded the subject of thermal decomposition; this is a field of investigation in which much work has been recorded in recent years. The influence of the temperature of formation has likewise been shown to have a considerable bearing on the physical properties of the resulting carbon; but most of these recent advances find no mention in the present volume. Likewise, the author's treatment of the subject of carbon black in compounded rubber is much too scanty, especially in view of the fact that the rubber industry is by far the largest user of the pigment.

In the chapters dealing with carbonaceous ink pigments and black paint pigments, there is little record of research of the past few years. The reviewer was responsible for a modest volume, "Blacks and Pitches," which appeared in 1925. It is curious to note many points of resemblance between this earlier volume and Dr. Mantell's. The concluding paragraph (7 lines) on p. 91 is almost identical with the third paragraph on p. 61 of the reviewer's book; the third paragraph (12 lines) on p. 94 of Dr. Mantell's book is identical, even to the extent of punctuation marks, with the second paragraph on p. 63 of the reviewer's book, whilst Table IV on p. 95 of the former is Table XV on p. 63 of the latter; even an error in copying in the latter appears in the former. Furthermore, the table and the concluding paragraph but one on p. 117 of the former book are, respectively, Table XII and last paragraph on p. 49 of "Blacks and Pitches." A numerical error in the last-named paragraph appears also in the corresponding paragraph of the former book. That two authors, unknown to each other, with an interval of four years between their efforts, and with the width of the Atlantic Ocean between them, should choose the same form of words in several paragraphs, and out of the mass of data available should each separately select in several tables identical particulars (with like errors in copying) is but another of those striking coincidences which from time to time break the monotony of life. Who shall have the temerity to deny that truth is indeed stranger than fiction?

The several chapters dealing with charcoal and decolorising carbons contain much useful information, though many recent researches in this connection appear to have escaped the author's attention. The short section dealing with the recovery of gasoline from natural gas is rather disappointing, particularly as coming from an American author, in view of the industrial importance of the subject. An important paper last year by Edeleanu, jun., on the application of this method in Roumania receives no mention in the volume under review.

The chapters devoted to carbon electrodes and allied manufactures are very detailed and appear well done, though there is an undoubted American bias in the treatment accorded. In Chapter XXIX the author has enumerated the chemical and physical properties of carbon, the references (to the total of 48) to the original sources of the data being given in each case. This tabulation will be found exceedingly useful.

The illustrations are good, though several of them are of plant now somewhat antiquated. The general style of the book is good, and the indexing has been carefully done. Should the author be called upon at a later date for a new edition it would be advisable that he should make himself familiar with the Journal of the Oil & Colour Chemists Association, with the Annual Reports on the Progress of Applied Chemistry, published by the Society of Chemical Industry, and with Chemical Abstracts in his own country. He will then be better able to give his readers up-to-date references to all recent work in the field he has chosen to describe.

H. M. LANGTON.

CHEMISTRY IN THE HOME. By J. B. FIRTH. First Edition. Pp. 246, with 17 illustrations. London: Constable & Co., Ltd. 1929. Price 5s. net.

This volume is an elementary text-book on hygiene, and is intended for the use of housewives, welfare workers and the teachers in girls' schools who have little or no knowledge of chemistry. It is divided into two parts, the first dealing with water, fuels, ventilation, lighting and other general subjects, whilst the second is devoted to foods and beverages.

To produce a volume of this nature for the use of the layman is by no means a simple matter, for, in addition to his natural difficulty in understanding a new subject, the reader is liable to misinterpret statements of fact and to arrive at false conclusions. The author has done his work in this respect very successfully, and, in spite of the wealth of material compressed into a small volume, his conciseness and freedom from ambiguity should prevent such consequences.

The author has devoted considerable industry to the compilation of the text, but has in some cases exceeded the limits of the title, for the formation of stalactites, lacustrine or oceanic salt deposits, and the manufacture of coal gas hardly come within the domain of home chemistry. Unfortunately many minor shortcomings are present which should have been corrected, and among the examples of bad grammar we find "This group of gases *are* known as the rare gases" (p. 14); and "the water can only retain the dissolved rock so long as *they keep* the carbon dioxide" (p. 35). Further, mis-spelt words are too frequent and include "epitheleum," "carbohdyrates," "Lilum" (of a starch grain), "pellogra," and others. Such faults would in some cases be detected and corrected by the readers, but the following incorrect statements of fact are likely to be accepted as true: "When nitrocellulose is dissolved in *ether*, it yields collodion" (p. 152); "Spermaceti, *an oil* obtained from the sperm whale" (p. 80); "Lysol contains cresol, castor oil and potassium hydroxide" (p. 116); "Apple *protein* is now a commercial article" (p. 191), and so on.

Apart from these errors, the volume contains much of general utility, but the material provided requires considerable dilution if the readers are to escape mental dyspepsia and the satiety induced by the acquisition of that little knowledge which so often proves dangerous. The illustrations are, on the whole, good and clear, but in Fig. 4 the vertical limbs of a syphon barometer are, in proportion, separated by a distance of a foot, and more interest would have been added to the micro-drawings of textile fibres, starches and yeast had the magnifications been given. The bacterial plate culture depicted in the frontispiece also requires fuller explanation. The page references in the text, numerical data and index are accurate; but the index, although containing over 360 items, is not sufficient to include the many varied matters dealt with in the book. In spite of its blemishes, the volume is far from being a failure, and the author has done well in producing a work of considerable interest and utilitarian value to those for whom it is intended, but a second edition should be submitted to decidedly more careful reading of the proofs. T. J. WARD.

CHEMISTRY OF PULP AND PAPER-MAKING. By EDWIN SUTERMEISTER, S.B. Second edition. Pp. x+565. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1929. Price 32s. 6d. net.

The second edition of this publication will be welcomed by all connected with the industry of pulp and paper-making. The name of Sutermeister in itself commands respect. The book, re-written in the light of knowledge gained since 1920 (date of first edition), only increases that respect. Lucidity, thoroughness, and a critical broad-mindedness are its characteristics.

A concise but comprehensive survey of cellulose, the basic raw material of the industry, a compound the constitution of which is still problematical, makes Chapter I a valuable guide to the seeker after up-to-date information on this substance and its reactions.

Under "Fibrous Raw Materials," an account is given of the vegetable cell, together with morphological, microscopical and other data for all the well-known paper-making fibres, including pulps from various woods. This section is admirably illustrated by photo-micrographs made for the Bureau of Standards.

The descriptions of the soda, sulphate, sulphite and mechanical processes for the preparation of wood pulps are supplemented by a very interesting chapter on the newer methods, *e.g.* the "Keebra," "Ramar," and "Explosion" processes. Another modern development described is the bleaching of pulp by liquid chlorine, and up-to-date methods for the evaluation of wood pulp for strength and beating properties are critically examined.

Regarding the vexed question of sizing paper, Sutermeister indicates that little help is to be obtained from a control of the P_H value of stock. His work suggests that the solution lies in drying and its effects; at the same time his attitude is by no means dogmatic. Sizing with such comparatively novel substances as sodium silicate and rubber latex is discussed; the claims originally made for the latter are shown to be much exaggerated, a fact in accordance with the reviewer's experience. Loading and filling materials are dealt with very fully, and the photo-micrographs in illustration should prove helpful to any analyst endeavouring to determine the type of filling present in a sample of paper. A simple apparatus for the determination of grit in fillers, by flotation, is described; this is a welcome alternative to the complicated elutriation usually recommended.

The colouring of paper with both inorganic pigments and organic dyes is usefully surveyed, and methods of determining the fastness of dyes to chemicals with which they come in contact, as well as some suggestions on the testing for fastness to light, are included. In discussing coated papers much valuable information is recorded on the testing and control of the materials used, *e.g.* glue, casein and other adhesives, blanc fixe, satin white, etc.

As regards the testing of paper, Sutermeister has adopted the methods of the Technical Association of the Pulp and Paper Industry. He gives only the essential

methods, however, and these in synopsis. While they are sufficiently full to meet the needs of routine work in a paper mill, the general analyst may desire a wider treatment. The references, however, do much to supply this minor deficiency.

In dealing with printing, the author points out defects giving rise to "complaints," and the possible faults of printer, paper-maker, and ink-maker, are enumerated. Anyone having to advise on printer's troubles should find this section helpful.

The appendix contains some useful physical data and conversion tables. The amount of data and the number of analytical methods included in the text, constitute distinctive features of this well-written and well-illustrated book.

WILLIAM DICKSON.

SHAKSPERE FORGERIES IN THE REVELS ACCOUNTS. By S. A. TANNENBAUM, M.D. Pp. 89, with 22 full-page facsimiles. New York: Columbia Press; London: Oxford University Press. Price 75s. net.

In these days of cheap mass-production of books it is a pleasure to meet with one so luxuriously produced as this volume. It is printed on good thick paper in bold clear type, and, although large, is easy to open and to hold, and the facsimiles of the original documents are admirably reproduced. The author, too, gains much by having his argument, which demands the closest attention, clothed in a form which attracts instead of repelling the reader.

The book deals with a controversy which is now more than sixty years old, but which, as the author shows, is still not closed. The story opens in 1842 with the alleged discovery in a cellar of Somerset House of the official books of the Revels Accounts for the years 1604–5 and 1611–12, by Peter Cunningham, a clerk in the Audit Office. As these accounts fix the date of some of Shakespeare's plays, they were at once accepted as a most valuable discovery, and a full transcript of them was published. Little more was heard of them until 1868, when Cunningham, who had by that time fallen a victim to drink, offered to sell them to the British Museum, but Sir F. Madden, the Keeper of the MSS. Department, claimed that the documents were already the property of the nation, and established the claim.

As soon as they were open to inspection doubts as to their being genuine were expressed, and positive opinions were put forward on each side. The controversy, an outline of which is given in this book, culminated in 1911, when Mr. Ernest Law obtained opinions on the writing from some of the leading palaeographers of the day, including Sir George Warner. As doubts had previously been expressed concerning the ink, Sir James Dobbie (then Government Chemist) was asked to apply chemical tests and to report upon it. Apparently it was tacitly accepted that only the lists of plays produced were open to suspicion, and that the rest of the documents was unquestionably ancient.

Dobbie's report, which is given here in full, was to the effect that his microscopical and chemical examination of the book of 1604–5 revealed no differences between the inks in any part of the document, and that there was no indication that the ink in one part had faded more than that in another, as was to be expected if part of the writing was 200 years old, whilst another portion had been written in or about 1868, as suggested.

This is probably the first instance where a chemist has been asked to assist in solving a literary problem, and the report has thus a special interest. The conclusions embodied in it are relative only, but Mr. Law has made use of it to support his view in a way which the report itself does not warrant. Thus he says that the ink has been demonstrated not to be modern in chemical constitution, and that it has been shown to be "absolutely ancient." Such distortions of the report of a chemist are not unknown in the fields of advertisement, but should not be brought into a literary and scientific controversy.

Largely owing to the stress laid upon this report and to the opinions of the palaeographers, the authenticity of these documents has now been generally accepted, although some faint voices of doubt have been heard.

In the present work, however, Dr. Tannenbaum brings many cogent arguments, illustrated by photographic reproductions, to prove that, after all, the Revels Accounts are forgeries. He condemns the opinions of the palaeographers on the ground that they had not the training to analyse variations in writing, and that they did not use the microscope, which would have shown the variations.

With regard to the chemical report, Dr. Tannenbaum asserts that the entire documents are forgeries, and that because the same kind of ink was used in different portions of a document, and apparently at the same time, it does not follow that the ink was ancient. Apart from that, he claims that some of the so-called "alterations," when examined under the microscope, show indications of having been made over original outlines, and that they are fraudulent emendations, not legitimate alterations.

It will thus be seen that several interesting scientific problems connected with these documents demand further work before they can be regarded as settled, but the author has undoubtedly made out a very strong case in support of his view, and his book will repay careful study by those who are even indirectly interested in his subject.

EDITOR.