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Tannin as a Selective Reagent for Zirconium

By W. R. SCHOELLER, Ph.D., F.R.I.C.

It will be recalled that in the course of our investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates,[1,2] we have introduced the use of tannin as a reagent of paramount importance for the quantitative separation and gravimetric determination of a number of elements. The principal applications proposed by us may be grouped under 4 heads according to the medium in which the reaction is made to take place: (1) In *oxalate soln.*, tantalum, titanium and niobium (Group A) are quantitatively separable from Group B (zirconium, thorium, aluminium, uranium, etc.)[3]; within Group A, tantalum is quantitatively separable from niobium.[4] (2) From neutralised *tartrate soln.*, tannin quantitatively ppts. all the above elements[5]; a number of others, beryllium, rare earths, manganese, etc. (Group C) are pptd. only from ammoniacal tartrate soln.[6] (3) A soln. of tannin in *dilute sulphuric acid*, in contact with a bisulphate melt, dissolves titanium, zirconium, and metals yielding soluble sulphates, leaving an insol. residue containing tantalum and niobium.[7] (4) *Hydrochloric acid* added to an alkaline tungstate soln. containing tannin ppts. the tungsten complex, cinchonine soln. being added for the sole purpose of completing its flocculation, *not* as a precipitant for tungstic acid (tannin-cinchonine method[8]). The present paper describes tannin reactions occurring in hydrochloric acid soln. and their bearing on the analytical chemistry of zirconium.

The tannin-cinchonine method provides a separation of tungsten from uranium, aluminium, and beryllium, if present in the alkaline soln., the tannin complexes of these elements being soluble in hydrochloric acid.[9] Zirconium, on the other hand, has been shown to interfere in the determination of tungsten by the same method in tungstate solns. containing a little sodium zirconate.[10] The positive tungsten errors were ascribed to zirconia "occluded in the tannin-cinchonine ppt." While re-investigating this rather unexpected result I found that zirconium chloride solns. containing free hydrochloric acid are actually pptd. by tannin, the ppt. flocculating readily and filtering well. Further study revealed that the pptn. is quantitative and affords a separation from many elements, the tannin complexes of which are soluble in acid.

Experimental—(1) *Gravimetric determination of Zirconium*—Two solns. of pure recrystallised zirconyl chloride in 0·1 *N* hydrochloric acid were standardised by pptn. with ammonia and ignition of the ppt. to ZrO_2; 25-ml portions gave 0·0521 and 0·0655 g respectively. The pptn. with tannin was carried out as follows: 25-ml portions were diluted to *ca.* 50 ml, heated to boiling, and treated with 10 ml of saturated ammonium chloride soln. and 1 g of tannin in strong freshly-made soln. The whitish flocculent ppts. were mixed with filter pulp, collected on 11-cm. No. 41 Whatman filters, washed with 2% ammonium chloride soln., and ignited to ZrO_2. Found, 0·0521 and 0·0654 g respectively, in excellent agreement with the values obtained by ammonia pptn.

(2) *Separations*—The tannin separation of zirconium from other metals hinges on the acidity of the soln., as was proved by the test separations described below, in which the zirconia was pptd. in presence of other metallic chlorides at relatively high concns. At or below 0·1 *N* acidity there is extensive co-pptn. of, *e.g.*, aluminium, while at higher acid concns. (*e.g.*, 0·5 *N*) the zirconia recovery is incomplete (*TP* = ignited tannin ppt.):

Expt.	ZrO_2, g	Al_2O_3, g	Acidity	*TP*	ZrO_2 Error, g
1	0·0521	0·3890	*ca.* 0·1 *N*	0·0725	+0·0204
2	0·0521	0·3890	*ca.* 0·5 *N*	0·0477	−0·0044

A separation method involving re-treatment of *TP* appeared undesirable, since this would require bisulphate fusion followed by conversion of the sulphate into chloride soln. I avoided

the re-treatment by pptng. the major zirconia fraction (TP^1) at 0·25 to 0·5 *N* acidity and recovering the balance (TP^2) from the filtrate by partial neutralisation. This simple procedure was found to yield uniformly good results.

Procedure—Treat the chloride soln. free from sulphate (0·1 g ZrO_2) with 20 ml of saturated ammonium chloride soln., dilute to 200 ml, and adjust the hydrochloric acid concn. to 0·25 *N* (if vanadium or thorium is present, to 0·5 *N*). Boil, stir, and add a freshly-made strong soln. of 1 g of tannin. Gently boil for 1 min., set aside to cool, collect after 2 hr. on an 11-cm. filter containing a little creamed filter-pulp, using a cold wash-liquor containing 50 ml of saturated ammonium chloride soln. and 25 ml of strong hydrochloric acid in 500 ml; measure the volume of this wash-liquor before and after use. Ignite the wet ppt., TP^1, in a tared porcelain crucible.

Minor zirconia fraction: the quantity of acid in the filtrate *plus* washings being known, stir the boiling liquid and add ammonia (1 : 1) so as to leave 2–3 ml of free acid (determine the equivalence of the strong acid and 1 : 1 ammonia used). As neutralisation proceeds the liquid becomes turbid, a delicate test for minute amounts of zirconia; flocculation normally occurs almost at once. If too much ammonia is added a heavy flocculent ppt. begins to form, which readily dissolves in a few ml of 1 : 1 hydrochloric acid kept ready at hand. Cool to room temperature, collect and wash the ppt. as before, ignite wet and weigh. The two ppts. may be ignited together or separately; I prefer the latter, should a purity test on TP^2 appear desirable.

Test separations—The above procedure gave the following results, the weight of metallic chloride added being calculated to oxide (except in Expt. 15):

Expt.	ZrO_2 taken	added		HCl concn.	TP^1	TP^2	ZrO_2 found	ZrO_2 Error
	g		g		g	g	g	g
3	0·0521	Al_2O_3	0·3890	0·25 *N*	0·0511	0·0014	0·0525	+0·0004
4	0·0521	Fe_2O_3	0·3600	do.	0·0500	0·0019	0·0519	−0·0002
5	0·0521	Cr_2O_3	0·2337	do.	0·0518	nil	0·0518	−0·0003
6	0·0655	R_2O_3*	0·2060	do.	0·0635	0·0014	0·0649	−0·0006
7	0·0521	U_3O_8	0·2800	do.	0·0516	0·0009	0·0525	+0·0004
8	0·0655	BeO	0·1185	do.	0·0615	0·0035	0·0650	−0·0005
9	0·0655	MnO	0·3140	do.	0·0642	0·0010	0·0652	−0·0003
10	0·0521	V_2O_4	0·2496	do.	0·0555	0·0012	0·0567	+0·0046
11	0·0521	do.	0·2496	0·5 *N*	0·0443	0·0078	0·0521	0·0000
12	0·0521	ThO_2	0·1005	0·25 *N*	0·0544	0·0041	0·0585	+0·0064
13	0·0655	do.	0·1005	0·5 *N*	0·0583	0·0122	0·0705	+0·0050
14	0·0655	do.	0·1005	do.	0·0561	0·0100	0·0661	+0·0006
15	0·0655	Ni	1·00	do.	0·0628	0·0024	0·0652	−0·0003

* R_2O_3 = 0·1046 g Nd_2O_3 + 0·1014 g Y_2O_3.

OBSERVATIONS—(1) *Separation from iron*—When tannin is added to the hot hydrochloric acid soln., the zirconium comes down as a brown ppt. The discoloration was at first believed to be caused by co-pptn. of iron, but on ignition the brown ppts. yield pure white ZrO_2; hence it must be due to an organic impurity in the reagent, probably oxidised by the ferric salt, since in the other test separations the zirconium ppts. were not unduly discoloured. As a general rule, elements with colourless tannin complexes give white ppts. which become buff or dirty white on further addition of reagent. Tannin added to hot acid ferric chloride solns. changes the colour to a reddish-brown, further addition of hydrochloric acid not restoring the original yellow colour. Dr. Nierenstein, whom I consulted on the question, suggests that these colour reactions may be due to the cyclogallipharic acid present in commercial tannins.*

(2) *From vanadium*—Solutions of vanadyl chloride were prepared from pure ammonium metavanadate by evaporation with strong hydrochloric acid. The separation must be carried out in 0·5 *N* acid (Expt. 11): at 0·25 *N* acidity a high result was obtained, and the ignited TP^1 was yellow (Expt. 10).

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* Cyclogallipharic acid, $C_{20}H_{34}.OH.COOH$ (Kunz-Krause, *J. prakt. Chem.*, 1904, **69**, 385, 387; Kunz-Krause and Richter, *J. prakt. Chem.*, 1907, **75**, 306; *Arch. Pharm.*, 1907, **245**, 28; Manicke, thesis, Dresden, 1910), crystallises from light petroleum in needles, m.p. 89° C. The cyclogallipharic acid placed by Heilbron and Bunbury (*Dictionary of Organic Compounds*) under the heading *Hydroginkolic Acid* is 6-hydroxy-2-pentadecylbenzoic acid. It contains in its molecule one C atom more than Kunz-Krause's compound and melts at 86°–88° C. These data are taken from *Sci. Papers, Inst. Phys. Chem. Res., Tokyo*; presumably the cyclogallipharic acid derived from Japanese galls differs from that from European galls.

(3) *From thorium*—As was to be expected, the separation of zirconium from thorium is slightly more delicate than the other operations here described. In Expt. 12, pptn. at 0·25 *N* acidity gave a positive error. In the next test (13), the higher acid concn. gave a TP^1 free from thoria; the positive error was incurred wholly in the recovery of TP^2 through over-neutralisation, which necessitated re-acidification. Once formed, the thorium complex evidently re-dissolves in acid more sluggishly than the other tannin complexes. It is therefore essential to conduct the partial neutralisation so that the soln. remains slightly acid; the volume of 1 : 1 ammonia required should be carefully calculated as prescribed, and a strip of litmus paper partly immersed in the soln. as a control. In Expt. 14, with an error of +0·0006 g, the combined ppts. gave a weak thorium reaction when the bisulphate melt was extracted with oxalic acid.[11]

(4) *From nickel*—This test separation from a large amount of nickel was undertaken with a view to using tannin in the determination of zirconium in materials subjected to sodium peroxide fusion in nickel crucibles. The separation was easily accomplished.

INTERFERENCES—Tantalum, niobium, and tungsten cannot normally be present in simple chloride solns. Tin[12] and titanium are pptd.; the tin complex appears to be more insoluble than those of zirconium and titanium. In acid solns. containing ferric chloride titanium yields a brownish-red ppt. of much darker hue than the vermilion complex obtained in oxalate or tartrate soln. Germanium gives a white tannin complex insoluble in dilute sulphuric acid,[13] the pptn. of which may serve for its separation from zirconium; hence germanium is no doubt pptd. by tannin from hydrochloric acid soln. However, it is so rare that the possibility of its association with zirconium in more than traces is quite remote. Stannic and germanic chlorides are volatile; the two metals can be pptd. as sulphides. As regards hafnium, we may take it for granted that it follows zirconium in this as in all its other reactions. The hafnium content of the zirconium preparation used in this work is not known to me, but it may be recorded that the salt was prepared from purified zircon sand derived from the Travancore beach deposit. Sulphuric acid or sulphates should not be present; the former prevents, the latter retard and impair pptn. To sum up, titanium is the one element that must always be tested and allowed for in zirconia obtained by tannin pptn., but this is the rule in zirconium analysis by other processes; if small, the titanium content is determined colorimetrically, if large, by the gravimetric tannin process in oxalate soln.[14]

ANALYTICAL APPLICATION—The quantitative pptn. of zirconium by tannin from acid chloride soln. is not merely of theoretical interest in establishing a new serial order of precipitability (probably Sn-Zr-Ti-Th-V-*M'''*-U-*M''*), as against the oxalate series,[15] Ta-Ti-Nb-V-Fe-Zr-Th-Al-U-*M''*. Tannin undoubtedly has certain practical advantages over other precipitants, which should secure its adoption as one of the selective reagents for zirconium; the operation is one of great simplicity, the reagent is cheap and stable and the ignition products of the ppt. are innocuous. Single pptn. separates zirconium from preponderating amounts of other metals; it is true that the recovery takes place in two fractions, but even so the operation is still simpler than, *e.g.*, the arsenate[16] or selenious acid[17] process, both of which involve double pptn. as well as conversion of the sulphate into chloride soln.

The zirconium-tannin complex produced in hydrochloric acid soln. contains less tannin and is less bulky than those pptd. from neutral or ammoniacal solns.; it flocculates readily, but hardly adheres to the glass at all. It includes any titania present, which must be determined and deducted. In the cupferron method[18] the zirconium ppt. contains the whole of the titania and minor quantities of thoria and rare earths. The ppt. obtained by the arsenate method[16] must be tested colorimetrically for titania. The selenite ppt.[17] includes any thoria present, and a colorimetric test for titania is advised. The phosphate method[19] is the only one that yields a zirconium ppt. quite free from titania; but it is unsuitable for substantial quantities, and the ignited ppt. is not of constant composition. On ignition the cupferron, arsenate, and selenite ppts. give off poisonous fumes.

This investigation is still in progress, and I hope to submit data on the tannin pptn. of titanium and tin from chloride solns., the treatment of sulphate solns., the resolution of Group B by tannin without the use of cupferron,[20] and the application of the tannin method in the analysis of zirconium ores.

SUMMARY—Zirconium is quantitatively pptd. by tannin from chloride soln. containing free hydrochloric acid below 0·1 *N* concentration. The reaction affords a separation of zirconium from sesquioxides, monoxides, uranium, vanadium, and thorium, the bulk of the zirconium being first pptd. at 0·025 to 0·5 *N* acidity, and the small balance in the filtrate by

partial neutralisation. Titanium and tin are pptd. with the zirconium. The advantages of tannin as a selective reagent for zirconium are discussed. The application of tannin in zirconium analysis is under investigation.

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THE TAPPING HOUSE
GREAT MISSENDEN, BUCKS.

June, 1944

A New Method for the Estimation of Micro Quantities of Cyanide and Thiocyanate

BY W. N. ALDRIDGE

INTRODUCTION—Many of the reactions for cyanide are either insensitive or of qualitative interest only, *e.g.*, the picric acid,[1] the Prussian blue[2] and the copper-benzidine[3] reactions. The method based on conversion of cyanide into thiocyanate[4] and determination of the thiocyanate by the ferric thiocyanate procedure, although of reasonable sensitivity, is extremely unreliable with small amounts of cyanide, owing largely to instability of the ferric thiocyanate colour. Of the other methods of sufficient sensitivity, the phenolphthalein[5] and the more recent *o*-cresolphthalein[6] methods, both require very careful control and are unspecific, the reduced form of these compounds being also oxidised by means other than cyanide. The method here described is based on the conversion of cyanide and thiocyanate into cyanogen bromide, which is then estimated by its colour reaction with amines in pyridine solution.[7]

METHOD—In neutral or acid soln. cyanide and thiocyanate are converted by bromine water into cyanogen bromide:

$$HCN + Br_2 = CNBr + HBr$$
$$KCNS + 4Br_2 + 4H_2O = KBr + CNBr + H_2SO_4 + 6HBr$$

The cyanogen bromide thus formed, after removal of excess of bromine with sodium arsenite, reacts with a solution of benzidine in dil. pyridine to give an intense orange to red colour proportional to the amount of cyanogen bromide present.

By this means 0·3μg of hydrocyanic acid and 0·6μg of thiocyanic acid may be easily and accurately estimated and the limit of detectibility on a rough qualitative basis is of the order of 0·05μg of HCN.

For the purpose for which the method was required, it was desired to differentiate between cyanide and thiocyanate. This may be easily achieved by making use of the non-volatility of thiocyanic acid.

Reagents—Bromine water—saturated. *Sodium arsenite soln.*—1·5% in water. *Pyridine reagent*—25 ml of pure redistilled pyridine, together with 2 ml of conc. hydrochloric acid, diluted to 100 ml with water. *Benzidine hydrochloride soln.*—2% in water.

Procedure—To 1 ml of the soln., containing up to 3μg of HCN or 6μg of HCNS and made acid with acetic or trichloroacetic acid, add 0·5 ml of saturated bromine water and then 0·5 ml of 1·5% sodium arsenite soln. At this stage the soln. may be left stoppered for 2 hr. Add 1 ml of this soln. to a mixture of 5 ml of the pyridine reagent and 0·2 ml of 2% benzidine hydrochloride soln. The orange colour immediately produced soon changes to a red. Allow 10 min. for colour development at room temp. and read the resulting colour on the Spekker Absorptiometer in 1-cm cells, using an Ilford micro 2·303 blue filter. Compare the result with a calibration curve prepared in an identical manner.

CYANIDE AND THIOCYANATE IN THE SAME SOLUTION—Thiocyanate and cyanide both react with bromine to give cyanogen bromide. If both are present, it might be important to differentiate between the two in view of the relatively low toxicity of thiocyanate as compared with cyanide.

Procedure—Cyanide may be easily removed by bubbling air through an acid soln. of thiocyanate and cyanide, leaving the thiocyanate unchanged. Two operations are necessary for the determination of both radicles—(1) Determine the Spekker reading for cyanide and thiocyanate together as above. (2) Bubble air saturated with water vapour through 1 ml of the soln. for 15 min. to remove cyanide and then continue in the usual manner for the thiocyanate. The reading obtained for (2) gives the thiocyanate present and the difference between the readings gives the cyanide present. Although throughout this work the readings were taken on the Spekker Absorptiometer, any other photoelectric instrument may be used.

EXPERIMENTAL—(1) *Calibration curves*—Solns. of cyanide and thiocyanate were standardised by the usual titrations with silver nitrate. Dilutions were then made to give the dil. solutions used for the calibration curves. Portions of these were submitted to the technique outlined above. A blank gave a zero reading.

HCN, μg	0	0·71	1·42	2·12	2·83	
Spekker reading ..	0	0·230	0·425	0·655	0·870	
HCNS, μg	0	1·24	2·48	3·72	4·96	6·20
Spekker reading ..	0	0·175	0·370	0·545	0·715	0·885

If the results for the thiocyanate curve are calculated to cyanide and plotted on the cyanide curve, the two curves coincide.

2. *Determination of thiocyanate and cyanide together*—The following results were obtained with known mixtures of thiocyanate and cyanide.

HCN present, μg ..	0	0·7	1·4	2·1	2·8	3·5
HCNS present, μg ..	10·3	8·25	6·2	4·1	2·05	0
HCN estimated, μg ..	0·01	0·6	1·3	2·2	2·8	3·5
HCNS estimated, μg ..	10·2	8·5	6·5	3·8	1·9	0

3. *Reaction of cyanogen halides with the pyridine reagent and benzidine*—Whilst both cyanogen chloride and bromide react with great speed with the reagent, cyanogen iodide reacts extremely slowly and is of no value for the estimation in hand. Cyanogen bromide has been chosen because its volatility (b.p. 61° C.) is lower than that of the corresponding chloride (b.p. 13° C.).

4. *Concentration of water in the colour development*—Known amounts of cyanogen bromide were added to a pyridine reagent containing various quantities of water. The colours developed were read immediately on the Spekker Absorptiometer, using an Ilford micro 2·303 blue filter.

Water, %	13	22	30	39	48	55	65	83	87
Spekker reading ..	1·02	1·06	1·07	1·08	1·08	1·09	1·10	1·10	1·10
Water, %	91	95							
Spekker reading ..	1·10	0·30							

The sensitivity is increased slightly down to a concn. of 10% of pyridine in water; further, in the dilute pyridine solns. the orange colour first formed rapidly changes to red at room temp., a change which is accelerated by hydrochloric acid in the pyridine soln. The change to red with 95% pyridine, with the subsequent increase in sensitivity, requires controlled heating in a water-bath.

A pyridine reagent was chosen containing 25% of pyridine and 2% v/v of conc. hydrochloric acid. The benzidine hydrochloride solution was added separately before each test as the composite reagent rapidly darkens.

5. *Conversion into cyanogen bromide*—(*a*) *Removal of excess bromine*—Excess of bromine reacts vigorously with the pyridine-benzidine reagent producing first the blue quinonoid compound which immediately decomposes with production of a dark brown colour. Any substance used for the removal of bromine must react in acid soln. (in alkaline solns. cyanogen bromide is converted into cyanate) and must also have no effect on the subsequent colour development.

Various substances ranging from inorganic reducing agents such as stannous chloride, sodium thiosulphate, sodium sulphite and sodium arsenite, to organic compounds such as metol, hydroquinone and 8-hydroxyquinoline were tried. All except sodium arsenite were rejected for one or both of the considerations mentioned.

(*b*) *Speed of conversion of cyanide into cyanogen bromide*—Slightly acid cyanide solns. were treated with bromine water and the excess was removed after various intervals of time by addition of sodium arsenite. The Spekker readings indicate that the reaction is almost instantaneous.

Time of bromination, min. ..	0	2	4	6	10
Spekker reading	0·695	0·690	0·700	0·690	0·690

(*c*) *Effect of excess sodium arsenite*—Different amounts of 1·5% sodium arsenite soln. (0·5 to 2·0 ml) were added to remove excess of bromine. The results indicate that a reasonable excess has no effect on the subsequent colour development.

Sodium arsenite, 1·5% soln., ml	0·5	1·0	1·5	2·0
Spekker reading	0·350	0·350	0·350	0·350

6. *Speed of colour development and stability of colour*—The colour developed was read after various intervals of time. The readings remained constant from 6 to 24 min. It should be noted that, although the colour alters markedly in shade during this period, there is no alteration in the extinction obtained with the blue filter.

Time, min.	0	2	4	6	8	10	12
Spekker reading	0·640	0·675	0·700	0·720	0·730	0·730	0·730
Time, min.		16	24	30	67		
Spekker reading		0·730	0·720	0·700	0·630		

7. *Effect of other substances on the determination*—Ferricyanides and cyanates have no effect, although it is certain that any compound that may produce CN′ or CNS′ radicles will be determined by this method. The indications are that organic cyanides and thiocyanates come into this class, although no quantitative examination has been made. None of the normal constituents of trichloroacetic acid blood filtrates has any adverse effect. The following substances also have no effect on the reaction:—potassium and sodium phosphates, ammonium and sodium chlorides, potassium oxalate, sodium borate, cobalt acetate in small quantities, phenyl acetic acid and ethyl alcohol. Oxidising and reducing agents present in small amounts will be removed by the sodium arsenite and bromine water respectively.

Application of the Determination to Biological Materials—The method given above can be readily adapted to the determination of cyanide and thiocyanate in biological materials. Both cyanide and thiocyanate may be determined in urine, and also in saliva in most instances without any preliminary treatment. Cyanide may be determined in whole blood, plasma or serum, and in pancreatic juice and other protein-containing fluids, after deproteinisation by means of trichloroacetic acid. Known amounts of cyanide were added to whole blood, 1 ml was deproteinised with 2 ml of 5% trichloroacetic acid, and the filtrate was analysed for cyanide as described.

HCN per μg of whole blood					
Added	6·33	11·6	16·07	17·48	19·9
Found	6·3	11·8	16·3	17·5	20·0

In plasma and other protein-containing fluids there was a 93% recovery of thiocyanate when no haemoglobin was present, but in acid deproteinisation of whole blood 80% of the thiocyanate is adsorbed by the ppt. As yet, no efficient method for the determination of thiocyanate in whole blood has been developed. In most instances, however, the determination in plasma is quite sufficient, as the thiocyanate appears to be evenly distributed between cells and plasma.

I am indebted to the Director-General, Scientific Research and Development, Ministry of Supply, for permission to publish this paper.

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CLATFORD OAKCUTTS
NEAR ANDOVER, HANTS

April, 1944

Mercuric Oxycyanide as a Reagent in Micro-analysis: Its Use in the Determination of Sulphur in Organic Substances, Ionic Halogen and Alkoxyl*

BY G. INGRAM

INTRODUCTION AND EXPERIMENTAL

SULPHUR—The Carius method for the gravimetric determination of sulphur is very accurate, but depends on such factors as complete oxidation, freedom from glass splinters when the bomb tube is opened, and complete precipitation of barium sulphate. Errors due to co-precipitation have been studied by Popoff and Neuman.[1]

Tetrahydroxyquinone[2] and sodium rhodizonate[3] have been used as indicators in titrating sulphate-ion with barium chloride soln. These indicators are satisfactory with 0·1 *N*, but tend to give inaccurate results with 0·01 *N* solns. owing to the difficulty of obtaining a correct end-point. This has been confirmed by Gibson and Caulfield.[4]

Methods have been described for determining the added excess of barium chloride by pptn. as chromate followed by iodimetric titration.[4,5] Manov and Kirk[6] have studied the errors—mainly due to occlusion—involved in this type of technique.

The combustion method of Pregl[7] provides a satisfactory method for the oxidation of organic compounds. When combined with a suitable titration procedure it has the advantage of quickness; and it is applicable to a larger range of compounds than the Carius method. There are, however, some disadvantages. Approx. 70% of the sulphur is converted into SO_3, which remains in the cool part of the combustion tube between the platinum contacts and spiral. The remaining 30% is converted into SO_2 and is retained by the spiral. This necessitates removal of the combustion tube from the furnace to enable the SO_3 to be washed out together with the soln. in the spiral in the final treatment. Loss of SO_3 also occurs when the compound explodes or burns rapidly, owing to the formation of mist, which readily passes through the absorbent soln. without being retained.

Two modifications have been described to enable the absorbed combustion products to be removed from the apparatus without removal of the latter from the furnace,[8,9] but both are unsatisfactory. In the former the SO_3 still remains in the combustion tube, and in the latter too much wash liquid is required.

In the present investigation errors due to (i) formation of SO_3 mist, (ii) design of the combustion apparatus, and (iii) gravimetric procedures, have been avoided (i) by carrying out the combustion in water-saturated oxygen, (ii) by re-designing the apparatus, and (iii) by utilising mercuric oxycyanide[10] to determine the excess of barium chloride.

Mist is prevented by the combination of SO_3 with water in the combustion tube to form sulphuric acid, which is trapped by the moistened glass beads in the lower portion of the combustion tube (Fig. 1, C). For this purpose an inlet wash tube is inserted above the moistened beads in the combustion tube, so that the sulphuric acid is conveniently removed with a few ml of wash liquid. The excess of barium chloride is determined with mercuric oxycyanide (introduced by Vieböck for halogen determinations) which reacts quantitatively as follows.

$$2Hg(OH)CN + BaCl_2 = 2HgCl.CN + Ba(OH)_2$$

* Read at the symposium held by the Microchemical Club, the South Yorkshire Section of the Royal Institute of Chemistry and the Sheffield Metallurgical Association, at Sheffield on October 9th, 1943.

Removal of Nitric Acid after Combustion.—Brewster and Rieman[11] have recently described a combustion procedure whereby nitrogen-containing compounds are analysed for sulphur by determining the sulphur as sulphuric acid after evaporating off the nitric acid produced by the combustion. Combustions by this procedure on compounds containing sulphur and nitrogen gave me inconsistent results. Loss of sulphuric acid on evaporation was suspected. To test this, solutions of 0·01 *N* sulphuric acid containing 2 ml of 0·01 *N* nitric acid or hydrochloric acid were evaporated on the water-bath. Loss occurred (possibly owing to creeping), its amount depending on the length of time the dishes were left on the water-bath after the bulk of the liquid had been removed. In these expts. the sulphuric acid was determined by direct titration with 0·01 *N* sodium hydroxide.

H_2SO_4 (0·01 *N*) taken ml	NaOH (0·01 *N*) required ml	Time on water-bath min.
5·47	5·44	5
5·47	5·43	10
5·47	5·38	20
5·47	5·31	30
5·47	5·29	40
5·47	4·91	50

Mixtures of 0·01 *N* sulphuric acid with excess of 0·01*N* barium chloride were evaporated, and the excess of chloride was determined, after removal of free hydrochloric acid by evaporation, by adding neutral mercuric oxycyanide reagent and titrating the liberated barium hydroxide with 0·01 *N* sulphuric acid. The following results were obtained.

H_2SO_4 taken ml	$BaCl_2$ taken ml	0·01 *N* H_2SO_4 for liberated $Ba(OH)_2$ ml	H_2SO_4 found ml
10·65	15·00	4·36	10·64
10·00	13·00	3·06	9·94
5·47	7·36	1·91	5·45
5·00	10·00	5·02	4·98
3·00	7·00	4·00	3·00
2·30	4·21	1·94	2·27
1·18	1·58	0·41	1·17
0·87	1·05	0·20	0·85
0·60	2·10	1·51	0·59
0·22	1·05	0·85	0·20

The following results obtained by evaporating sulphuric acid solns. containing 0·5 ml of conc. nitric and hydrochloric acids, respectively, and leaving them on the water-bath for 5 min. after the bulk of the soln. was removed, show that under these conditions the volatile mineral acids are removed completely, without loss of sulphuric acid, and do not interfere with the subsequent titration. In these expts. the sulphuric acid was determined by direct titration with 0·01 *N* barium chloride after addition of 10 ml of neutral mercuric oxycyanide reagent.

	0·01 *N* H_2SO taken ml	0·01 *N* $BaCl_2$ required ml
0·5 ml HNO_3	5·47	5·44
	5·47	5·46
0·5 ml HCl	5·47	5·45
	5·47	5·43

The titration procedure evolved for the combustion determination can be adapted, therefore, to the Carius oxidation method. The following table gives the % of sulphur found in various substances by Carius oxidation and by combustion.

Substance	Carius	Combustion	Theory
Sulphonal	28·24	28·2	28·1
	28·06	28·05	28·1
dl-Methionine	19·96*	21·41	21·5
	—	21·7	21·5
N^4-Acetyl sulphanilamide	15·2	15·2	15·0
N^4-Methyl sulphanilamide	17·5	17·32	17·2
Sulphur	—	100·1	100·0

* Low owing to incomplete oxidation.

HALOGENS—Organic ionic halogen compounds have been analysed successfully by dissolving in a suitable solvent, adding mercuric oxycyanide reagent, and titrating the liberated hydroxy compound with standard sulphuric acid.

ALKOXYL GROUPS—Attempts to use this reagent in the determination of methoxy and ethoxy groups were successful. The alkyl iodides were absorbed in pyridine[12] in a modified Zeisel apparatus (Fig. 3) fitted with a water condenser.[13]

THE METHODS

REAGENTS—*Mercuric oxycyanide*—Shake 20 g with 1 litre of water, and filter into a brown bottle; as the solution is slightly alkaline, neutralise each 10 ml used for the determination with 0·01 *N* sulphuric acid, using 4 drops of methyl red and 2 drops of methylene blue indicator solns. *Mixed indicator solutions*—Dissolve 50 mg of methyl red in 100 ml of alcohol and 50 mg of methylene blue in 100 ml of alcohol; keep both solns. in dropping bottles and add separately for each titration. *Hydrogen peroxide solution*—Dissolve 5 drops of 100 vol. peroxide in 10 ml of water and neutralise with sodium hydroxide soln., using 2 drops of methyl red as indicator. *Sodium bisulphite mixture*—Add 5 drops each of sat. solns. of sodium bisulphite and carbonate to 10 ml of water. *Sulphuric acid, Sodium hydroxide, Barium chloride*—0·01 *N* solns. of each. *Sodium hydroxide*—0·2 *N*. *Hydrochloric acid*—0·1 *N*. *Barium chloride* ($BaCl_2.2H_2O$)—Analytical Reagent quality.

THE COMBUSTION APPARATUS—The combustion apparatus (Fig. 1) consists of a Pregl pressure regulator, a preheater, a bubbler containing water, and a quartz combustion tube fitted with a side-arm, all mounted together on a stand. Connections between the preheater, bubbler and combustion tube are made by B.10 ground joints, lubricated with phosphoric acid and secured by springs. The preheater serves to heat the oxygen before it passes through the bubbler, thereby saturating the gas stream with moisture before it enters the combustion tube. The oxygen may be by-passed by means of the two-way tap sealed to the bubbler.

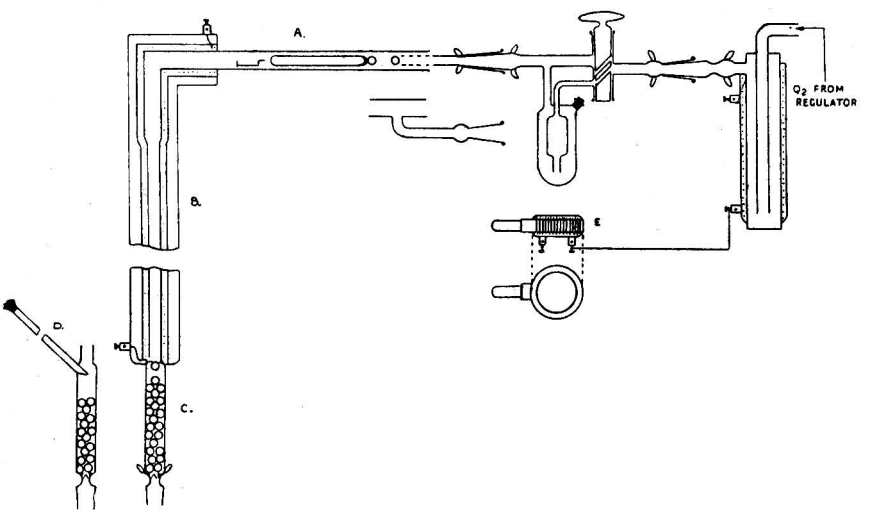

Fig. 1. Combustion Apparatus

The combustion tube is bent at right angles 20 cm from the mouth, fused together with an angle joint. The horizontal part A contains the combustion boat and quartz baffle, and the vertical part B the platinum contact (10 cm long) 25 cm from the bend; at the exit end is a tube C, 8 cm long, filled with glass beads, at the end of which an A.10 male joint is sealed. The inlet tube D, 10 cm long and 4 mm in diam., is sealed at the junction of the bead tube and combustion tube, and protrudes half way into the former in the form of a jet. The open end is closed by a rubber stopper.

That portion containing the contact and 5 cm of the horizontal part adjacent to the bend is covered with wet asbestos paper and wound with nichrome wire. This is covered with 5 more layers of wet asbestos and then wound with thick asbestos string, so that a compact insulated cover is provided. The combustion tube is then left in the oven until the

covering is dry. The preheater, which is treated in a similar way, is filled with a 50 : 50 mixture of cerium dioxide and lead chromate suspended on pumice stone (10–14 mesh).

The SO_2 absorber (Fig. 2) is U-shaped, with a tap sealed on at the bottom to facilitate

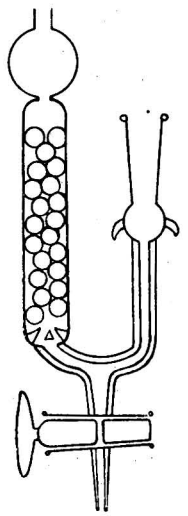

Fig. 2. Absorber for Combustion Apparatus

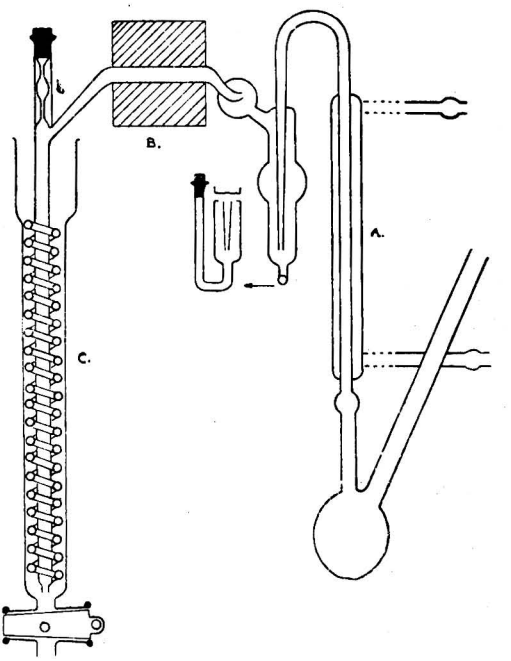

Fig. 3. Zeisel Apparatus
A—Water jacket B—Cork C—Pyridine absorber

washing. One arm, 7 cm long, of thick walled 2 mm bore tubing has a B.10 female joint sealed on for connection to the combustion tube. The other arm, which is 7 cm long and 11 mm in diam., is filled with glass beads; its upper outlet is constricted and terminates with a splash bulb 14 mm in diam.

GENERAL COMBUSTION PROCEDURE—Assemble the clean and dry apparatus and regulate the temperature of the furnace and preheater by rheostats, the former to 800° C. and the latter to 350° C. Fill the bubbler to the bulb of the inlet tube with water, and regulate the oxygen to a flow rate of 20 ml per min. to fill the combustion tube with water vapour. This can be accelerated by warming the bubbler slightly with the small electric heater (E).

Charge the absorber with 1·2 ml of absorbent soln. (neutral hydrogen peroxide for sulphur, sodium bisulphite mixture for halogen) and connect it to the combustion tube. Introduce the weighed sample and baffle and start the combustion, using a gas burner to drive the substance into the main heated part of the tube; *ca.* 10 min. will be required. After a further 10 min. turn off the oxygen, and determine the sulphuric acid by one of the following three procedures.

(1) *For sulphur in compounds containing no nitrogen or halogens*[14]—Remove the absorber and rinse the contents, together with the bead tube, with water into a 150-ml conical flask. Boil for 7 sec., cool, add 4 drops of methyl red and 2 drops of methylene blue indicator, and titrate with 0·01 *N* sodium hydroxide (1 ml of 0·01 *N* NaOH ≡ 0·1603 mg of S). As already indicated, 0·01 *N* barium chloride can be used as a stable standard soln. instead of 0·01 *N* sodium hydroxide (see p. 266).

(2) *For sulphur in compounds containing halogen*[4,15]—If the compound contains nitrogen also, use the procedure described in (3). If no nitrogen is present both sulphur and halogen are determined. Neutralise the soln. in the conical flask with 0·01 *N* sodium hydroxide; this gives the total acid. Add 10 ml of mercuric oxycyanide reagent and titrate the liberated alkali with standard sulphuric acid; this gives the equivalent of halogen (Cl or Br) present. Subtract this titre from the total acid titre to obtain the sulphur equivalent.

(3) *For sulphur in nitrogen-containing compounds*—Evaporate the absorbent solution and

washings (approx. 25 ml) contained in the evaporating dish on the water-bath until almost dry. Add 1 ml of 0·1 *N* hydrochloric acid and a known weight of solid barium chloride (20–50 mg) and again evaporate. Add 4 ml of water and evaporate to remove any free acid. Rinse the mixture of solid barium sulphate and chloride into a 150-ml conical flask, add 10 ml of neutral mercuric oxycyanide soln., and titrate the liberated alkali with *N* 0·01 sulphuric acid.

Use the same procedure for the Carius method. Rinse the contents of the bomb tube into the evaporating dish and evaporate. Then add barium chloride and continue as described above.

Halogen by combustion (*Chlorine and Bromine*)—Use the same combustion apparatus. Charge the absorber with 1·2 ml of sodium bisulphite mixture and rinse the liquid containing absorbed halogen acids into the conical flask. Add 3 drops of 100 vol. hydrogen peroxide to oxidise the bisulphite, boil for 2 min., cool, neutralise with 0·2 *N* sodium hydroxide, adjusting the neutral point with 0·01 *N* sulphuric acid, add 10 ml of oxycyanide reagent, and titrate the liberated alkali.

IONIC HALOGEN (CHLORINE, BROMINE AND IODINE)—Dissolve 3–10 mg of the substance in a suitable solvent, *e.g.*, water, add 10 ml of the reagent, and titrate the liberated hydroxyl compound with 0·01 *N* sulphuric acid. Boil compounds insoluble in water and dil. alcohol with 10 ml of 0·01 *N* NaOH sol., cool and neutralise before treatment with the reagent.

ALKOXYL—Use the normal procedure with the apparatus shown (Fig. 3). Transfer the pyridine containing the absorbed alkyl iodide to a 100-ml round-bottomed flask fitted with an outlet tube for connection to the water-pump, and an inlet tube reaching halfway into the flask. Distil off the pyridine under reduced pressure on the water-bath and dissolve the residue of pyridinium iodide in 5 ml of water. Add 10 ml of oxycyanide reagent soln. and titrate the liberated pyridinium base with 0·01 *N* sulphuric acid (1 ml of 0·01 *N* $H_2SO_4 \equiv$ 0·3100 mg of OCH_3 or 0·4500 mg of OC_2H_5).

SUMMARY—The technique described for sulphur determinations was developed to enable a titration procedure to be carried out on compounds containing nitrogen also.

By evaporating mixtures of *N*/100 solns. of nitric and sulphuric acids on the water-bath it was found that the former is removed completely with only slight loss of sulphuric acid. This loss depends on the length of time the acid is left on the water-bath after the bulk of the solution has been removed by evaporation. If prolonged heating is avoided at this stage the sulphuric acid can be accurately determined by titration with alkali.

An alternative method is described in which excess of barium chloride is added and after evaporation the excess is determined with mercuric oxycyanide. The method can be applied with equal accuracy to Carius sulphur determinations. It has the advantage of speed over the gravimetric method.

The combustion apparatus is modified so that errors due to the formation of SO_3 are eliminated.

The use of mercuric oxycyanide has been extended to the determination of ionic halogen, and to the Zeisel method, thereby replacing the gravimetric procedure by a rapid and simple acid-alkaline titration.

I am indebted to the Director General of Scientific Research and Development, Ministry of Supply, for permission to publish this paper.

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Notes

THE DETERMINATION OF SMALL AMOUNTS OF SILVER IN COPPER AND BRASS*

THE following investigation was undertaken to meet a demand for accurate information respecting the amount of certain low percentages of silver in copper and some copper alloys. It was found unnecessary to go outside the classical precipitation as chloride, and within the acidity and amount of chloride prescribed precipitation appeared to be complete. It was necessary to work on a large sample and the final determination was done cyanometrically. The following method was worked out.

METHOD—Dissolve 50 g of the sample (cleaned by pickling) in 200 ml of nitric acid (sp. gr. 1·42); it is better to have the sample in lump form and it is desirable to add the acid a little at a time. After action has practically ceased add a further 50 ml of nitric acid (sp.gr. 1·2), which will dissolve the remainder of the sample; boil out the nitrous fumes and dilute with 100 ml of hot water. Add 5 ml of 20% sodium chloride soln., boil for 10 min. and leave overnight. Filter off the pptd. silver chloride, cold, on a tightly pressed pulp filter and wash with cold water until copper is completely removed; then, having rinsed the outside of the funnel and stem to remove splashes, transfer it to a clean flask. Remove any adherent ppt. from the precipitation beaker by rinsing with 20 ml of dil. (1 : 3) ammonia, pouring these rinsings through the ppt. on the filter and wash two or three times with water; wash once with 20 ml of boiling dilute nitric acid (sp.gr. 1·2) and again two or three times with water. Finally remove all residual traces of silver from the filter by a second treatment with 20 ml of 1 : 3 ammonia followed by a third washing with water. Neutralise the filtrate with ammonia or nitric acid as required and add an excess of 10 ml of 1 : 1 ammonia; dilute the filtrate, which should be quite bright, to 200 ml and cool.

Titration—Run in an excess (say, *ca.* 10 ml) of standard potassium cyanide soln., add 10 ml of 4% potassium iodide soln. and titrate carefully to the first faint permanent opalescence with standard silver nitrate soln. The silver equivalent of the potassium cyanide is found by adding a measured vol. of cyanide soln. to the exactly titrated soln. and again titrating; if this volume is the same as that used originally it saves any need of factors in the conversion. The difference between the silver equivalent of the potassium cyanide originally used and that of the silver soln. required in the titration gives a measure of the silver present.

Trials made by this method with two samples of pure copper to which varying amounts of silver had been added gave the following results.

Material	Wt. taken g	Silver added g	Titration $AgNO_3$ soln. ml	Silver found (corr. for blank) g	Silver: Added %	Silver: Found %
Copper A	50·0	—	5·10 − 5·10 = —	—	—	—
,, ,,	50·0	0·00184	5·00 − 4·50 = 0·50	0·00184	0·00368	0·00368
,, ,,	50·0	0·00368	5·10 − 4·10 = 1·00	0·00368	0·00736	0·00736
,, B	50·0	0·00184	5·10 − 4·50 = 0·50*	0·00184	0·00368	0·00368
,, ,,	50·0	0·00368	4·90 − 3·80 = 1·00*	0·00368	0·00736	0·00736
,, ,,	50·0	0·00736	5·05 − 2·95 = 2·00*	0·00736	0·01472	0·01472
,, ,,	50·0	0·02945	11·00 − 2·90 = 8·00*	0·02945	0·05890	0·05890
,, ,,	50·0	—	5·00 − 4·90 = 0·10	—	—	—

* Corrected for blank.

Solutions used—(i) Potassium Cyanide—16·8 g of AnalaR potassium cyanide and 8·0 g of potassium hydroxide dissolved in water and made up to 3·5 litres.

(ii) Silver Nitrate (1 ml = 0·00368 g of Ag) — 11·584 g of silver nitrate dissolved and made up to 2 litres with distilled water.

Similar trials with two samples of brass, one 70 : 30 and the other 60 : 40 containing 2·30% of lead and 0·23% of tin gave:

Material	Wt. taken g	Silver added g	Titration ml $AgNO_3$ soln.	Silver found g corr. for blank	Per cent. of silver: Added	Per cent. of silver: Found
70:30 Brass	50·0	—	5·50 − 5·35 = 0·15	—	—	—
,,	50·0	0·00184	4·50 − 3·80 = 0·70	0·00202	0·00368	0·00404
,,	50·0	0·00368	5·30 − 4·15 = 1·15	0·00368	0·00736	0·00736
,,	50·0	0·00736	8·70 − 6·50 = 2·20	0·00755	0·01472	0·01510
,,	50·0	0·01472	6·75 − 2·60 = 4·15	0·01472	0·02944	0·02944
60:40 Brass	50·0	—	5·50 − 4·70 = 0·80	—	—	—
,,	50·0	0·00184	5·25 − 3·95 = 1·30	0·00184	0·00368	0·00368
,,	50·0	0·00368	4·40 − 2·60 = 1·80	0·00368	0·00736	0·00736
,,	50·0	0·00736	4·70 − 1·90 = 2·80	0·00736	0·01472	0·01472
,,	50·0	0·01472	6·50 − 1·75 = 4·75	0·01453	0·02944	0·02906

Large weights of both brass samples were dissolved, made up to a known volume and an aliquot part taken before the addition of the silver. This procedure was adopted because of earlier slightly erratic results obtained for the blank by taking separate sample weights. The only explanation of this would appear to be segregation of the silver present in the brass, although apparently there is no metallurgical support for this. "Metastannic acid" had to be filtered off from the 60 : 40 solution before proceeding.

The author wishes to thank the Director-General of Scientific Research and Development, Ministry of Supply, for permission to publish this paper.

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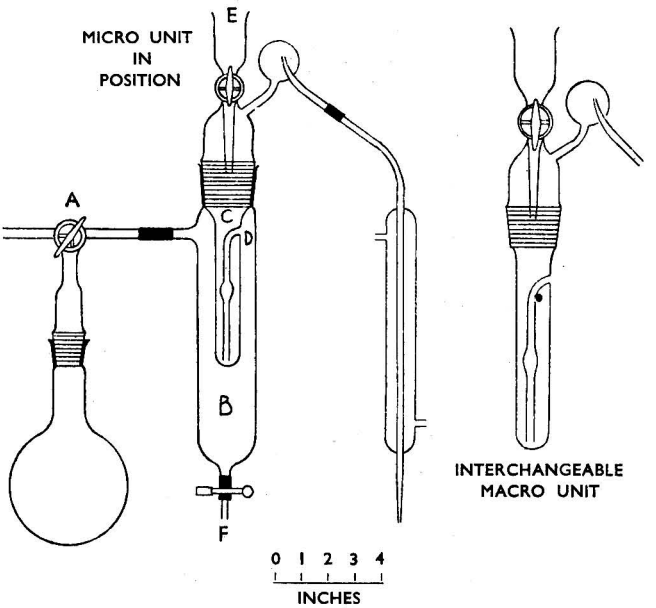
July, 1944

* Communication from Armament Research Department, formerly the Research Department, Woolwich.

AN INTERCHANGEABLE MICRO AND MACRO STEAM DISTILLATION APPARATUS

MANY types of Kjeldahl apparatus have been devised; in this note a new steam distillation apparatus is described, suitable for either micro or macro determinations. It incorporates an automatic emptying device, which makes it particularly suitable for serial analysis. Standard joints are used throughout, making for easy replacement. There are only two rubber connections, which minimises possible leakage of ammonia and permits the apparatus to be taken to pieces in less than 30 sec. for cleaning.

The apparatus consists of a boiling-flask fitted with a two-way stop-cock A, which is connected to a large outer chamber B, having at the bottom an outlet fitted with a pinch-cock F. Into the outer chamber is fitted either a micro- or macro "unit" according to the volume of the test solution. The unit consists of small chamber C, which communicates with the outer chamber by means of a tube D. Into the top of the "unit" is sealed a reservoir E and a trap connected with a condenser.



Procedure—Fix the pinch-cock F in the open position and pass the test soln. into the inner chamber via the reservoir E, rinsing it in with a few ml of water. Place a flask containing standard acid under the condenser so that the end of the condenser dips into the acid. Pass steam into the outer chamber B by turning the stop-cock A, close the pinch-cock F and add an excess of caustic soda soln. via the reservoir E. Continue distillation for 5 min. and then remove the receiver flask and rinse the end of the condenser into the acid. Turn the stop-cock A so that steam is cut off from the outer chamber and the contents of the inner chamber are slowly sucked into the outer chamber by the partial vacuum created by the steam condensing in the outer chamber. Pass 20 ml of water into the inner chamber via the reservoir E so as immediately to suck over and remove any remaining caustic soda from the apparatus. Draw off the finished solution by means of the pinch-cock F, leaving the apparatus ready for the next determination.

Once the correct pressure of steam suitable for the apparatus has been found the pressure need not be varied during the whole operation. It is essential to have a pressure of steam passing into the outer chamber while the solution is passing through the reservoir, in order to prevent siphoning of the solution from the inner into the outer chamber.

The chamber of the micro "unit" can accommodate and distil a total volume of 40 ml and that of the macro "unit" a total volume of 80 ml. Apparatus made and supplied by A. Gallenkamp & Co., Ltd.

LITTLE LAVENDER, ORCHARD ROAD
PRATT'S BOTTOM, KENT

J. L. HOSKINS

May, 1944

ISOLATION OF ERGOMETRINE FROM NEW ZEALAND FESTUCA ERGOT

DURING an extensive investigation of ergot alkaloids Smith and Timmis[1] examined some *Festuca* ergots, collected in New Zealand between 1927 and 1929, and reported the presence of ergotamine and ergotaminine in contrast to ergotoxine and ergotinine which they found, without exception, in all specimens of official ergot of rye examined.

The manufacture of ergotamine from a large batch of New Zealand *Festuca* ergot has afforded an opportunity for a more detailed study. The ergot in question was found by colorimetric assay to contain 0·59% of total alkaloid (calculated as ergotoxine) of which 0·03% was present as water-soluble alkaloid (calculated as ergometrine).

From the water insoluble alkaloidal fraction were isolated both ergotamine ($[\alpha]^{20}_{5461}$ — 165° for c = 0·3% in chloroform. Found: C, 68·63; H, 6·33; N, 12·02. Calc. for $C_{33}H_{35}O_5N_5$: C, 68·15; H, 6·07; N, 12·04%) and ergotaminine ($[\alpha]^{20}_{5461}$ + 465° for c = 0·3% in chloroform). These bases were interconvertible.

When the water-soluble fraction of the alkaloids was worked up by the usual process for the manufacture of ergometrine there was obtained a small quantity of crystalline alkaloid ($[\alpha]^{20}_{5461}$ + 64·5° for c = 1·5% in alcohol; m.p. 163° C. with decomposition. Found: C, 70·2; H, 7·4; N, 12·9. Calc. for $C_{19}H_{23}O_2N_3$: C, 70·1; H, 7·1; N, 12·9%). When compared colorimetrically with an authentic specimen of ergometrine it yielded quantitatively the same colour. There is no doubt that the alkaloid was ergometrine.

Although too little ergometrine was present for the *Festuca* ergot to be used as a source of the alkaloid, its presence in this variety of ergot is a matter of interest, as we believe it has not previously been found accompanying ergotamine and ergotaminine.

We wish to thank Mr. A. Bennett for the micro analyses and the Directors of the Wellcome Foundation for permission to publish this note.

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WELLCOME CHEMICAL WORKS
DARTFORD

G. E. FOSTER
R. L. GRANT

July, 1944

RHODAMINE B AS A SUBSTITUENT FOR CINCHONINE IN TUNGSTEN DETERMINATION*

IN view of the war-time shortage of cinchonine, it has been proposed to use rhodamine B instead as a precipitant for small amounts of tungsten.[1] The experiments described below were carried out to test the relative efficacy of the two reagents. As is well known, cinchonine is by no means a perfect precipitant where the amount of tungsten is very low; it was not to be demanded therefore that rhodamine B, as a substitute, should give theoretical results for quantities for which cinchonine showed low ones. On the other hand, Schoeller and Jahn[2] have shown that cinchonine used in conjunction with tannin can be made to precipitate tungsten completely from relatively strong solns. of alkali salts; it seemed worth while therefore to try if rhodamine B could replace cinchonine for this purpose also. The following expts. were made.

(*a*) Determination of known amounts of tungsten, added to electrolytic iron: (i) by the procedure of Gregory and Stevenson[3]; (ii) by exactly the same procedure but using 20 ml of 1% rhodamine B soln. in place of 10 ml of 5% cinchonine soln.

The following results were obtained.

Weight of iron taken, g	Weight of tungsten added, g	Reagent	Weight of WO_3 found	Tungsten, % Added	Tungsten, % Found
5·0	0·0025	Cinchonine	0·0033 − 0·0012 = 0·0021	0·050	0·033
5·0	0·0025	Rhodamine B	0·0044 − 0·0018 = 0·0026	0·050	0·040
5·0	0·0035	Cinchonine	0·0053 − 0·0012 = 0·0041	0·070	0·065
5·0	0·0035	Rhodamine B	0·0052 − 0·0014 = 0·0038	0·070	0·060
5·0	0·0050	Cinchonine	0·0055 − 0·0010 = 0·0045	0·100	0·071
5·0	0·0050	Rhodamine B	0·0062 − 0·0004 = 0·0058	0·100	0·092
5·0	0·0100	Cinchonine	0·0125 − 0·0008 = 0·0117	0·200	0·186
5·0	0·0100	Rhodamine B	0·0133 − 0·0010 = 0·0123	0·200	0·195

(*b*) Recovery of tungsten from strong solutions of alkali salts: (i) by Schoeller and Jahn's process[2]; (ii) by the same process with substitution of 5 ml of 1% rhodamine B soln. for 5 ml of 5% cinchonine soln.

In each expt. a measured volume of standard sodium tungstate soln. was added to a soln. containing 15 g of sodium sulphate, 10 g of sodium chloride and 5 g of potassium sulphate.

Results were as follows.

Tungsten added g	Tungsten found, g: Cinchonine	Tungsten found, g: Rhodamine
0·0200	0·0193	0·0207
0·0151	0·0151	0·0150
0·0100	0·0103	0·0101

From the above figures it would seem that, although neither reagent is perfect, rhodamine B can be used as a substitute for cinchonine in both the methods of precipitation of tungsten in which that reagent is normally employed. The results with rhodamine B are, if anything, a little better than those with cinchonine.

I wish to thank the Director General of Scientific Research and Development for permission to publish this note.

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CHEMICAL DIFFERENTIATION OF GALLS

STOCKERT and Zellner[1] were the first to draw attention to the presence of nitrogen in carbon tetrachloride extracts of galls, and subsequently Nierenstein[2] identified galloyl-leucine in similar extracts of Knopper galls. As the identification of galls by biological methods is somewhat tedious, we evolved a chemical method based on the above observations.† Of the 94 kinds of galls that we examined, 47 contained alanine,

* Communication from The Armament Research Department, formerly The Research Department, Woolwich.

† My collaborator, Dr. K. von Stockert, was killed in action in the last war. The present note embodies our results, which have not previously been published.—M. N.

26 valine and 21 leucine. The complete list of galls examined is to be published elsewhere, but it might be mentioned here that Bassorah, Chinese and Japanese galls contain alanine, that Knopper galls yield valine, and that English oak apples contain leucine.

The finely powdered galls were extracted in a Soxhlet extractor first with a mixture of carbon tetrachloride and chloroform (1 : 1) and then with alcohol. The residue left on evaporation of the alcoholic extract was dissolved in benzene and the soln. was filtered, diluted with light petroleum and left for 48 hr. in an ice-chest. The powdery ppt. crystallised from alcohol in small crystals which did not show a sharp m.p., being mixtures of the *l-* and *dl-* forms of the compounds, as had been observed by Nierenstein. For the purpose in hand this was not material.

The galloyl amino acids were hydrolysed as follows. One g of the product was suspended in 150 ml of $N/10$ sodium hydroxide and heated on a boiling water-bath for 3–4 hr., hydrogen being passed through the liquid throughout the hydrolysis and during cooling. The soln. was then transferred to a long, narrow separating funnel and a 1% soln. of copper sulphate was added until the liquid remained blue. The blue copper salt of the amino acid, which separated on standing, was slowly drawn off. It was freed from copper by means of hydrogen sulphide and the soln. was boiled for some time and filtered from sulphur. The cold soln. was treated by the method of Fischer and Bergel[3] to convert the amino acid into the corresponding amino-β-naphthalene sulpho derivative, and either the nitrogen or the sulphur in this was determined. The theoretical contents are:

Compound of	Nitrogen, %	Sulphur, %
Alanine	5·38	11·57
Valine	4·93	11·27
Leucine	4·69	10·79

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THE UNIVERSITY
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July, 1944

Ministry of Food

STATUTORY RULES AND ORDERS*

1944 No. 738. The Labelling of Food Order, 1944. Dated June 29, 1944. Price 3d.

This Order implements the policy announced in pars. 8 and 9 of the White Paper on the Labelling and Advertising of Foods (Cmd. 6482). It specifies the information which must be given on the labels of prepacked foods when sold by retail. *This information includes the name and business address of either the packer or the labeller of the food*; *also* the common or usual name (if any) of the food and also, in the case of a food made of two or more ingredients, the common or usual name of each ingredient, and the name of an ingredient shall be a specific, and not a generic name, and the ingredients shall be named in the order of the proportion in which they were used, the ingredient used in the greatest proportion (by weight) being named first. Provided that (*a*) it shall not be necessary to state that the food contains water; (*b*) where a food contains an ingredient which is made from two or more constituents, those constituents shall be specified and it shall not be necessary to specify that ingredient.

In the case of sales otherwise than by retail the same requirements apply or alternatively the food must be sold unlabelled and the purchaser supplied with a statement giving the required information.

Special requirements apply to the disclosures of the vitamin or mineral content of the food for which claims are made either in advertisements or on labels suggesting that the food contains these substances.

Foods exempted from one or more of the labelling requirements are listed in the First Schedule to the Order.

The procedure as regards entry and inspection of premises and taking samples, applicable for the purposes of this Order, is that contained in the Defence (Sale of Food) Regulations, 1943s Appropriate defences, including a defence similar to that provided by the Food and Drug. Act, 1938, where some other person is responsible for the commission of an alleged offence, are available in proceedings for an infringement of the Order.

— **No. 763. The Meat Products, Canned Soup and Canned Meat (Control and Maximum Prices) Order, 1944. Dated July 3, 1944.** Price 5d.

The new Order (*which came into force on July* 9) *is a consolidating Order.* It provides for the increase of the meat content of pork sausage and pork sausage meat (including pork slicing sausage) from 37½% to 50% (with a tolerance of margin of 2½% below and 5% above). The meat content of beef sausage and beef sausage meat (including beef slicing sausage) will remain 37½%. The inclusion of 7½% of low fat soya in pork and beef sausage and sausage meat is maintained in the new Order, which prohibits the use of any other soya product in pork and beef sausage and sausage meat, and of certain named offals.

* Obtainable from H.M. Stationery Office. Italics signify changed wording.

The meat content of meat paste is standardised at 55%, and the fish content of fish paste is increased to 70% (with a tolerance or margin of 5% above and below each figure); the increased content will apply equally to paste in airtight containers and to "open" pack pastes, except that it will be permissible to continue manufacturing the former to the old specification until July 30, 1944.

Pork slicing sausage and beef slicing sausage are included among the specified foods in the new Order. Hogs pudding and haslet or aislet are now included in the list of excepted products.

The Order provides that the minimum "solid" content of canned soup shall not include bone. *The min. standards of quality are as follows.*

Variety of soup	Solids, %	Protein, %	Fat, %
Meat	12	2½	—
Mulligatawny ..	13	2	2
Cream	10	—	3½
Vegetable	10	1	—
Clear	7	6	—

1944 No. 798. The Fruit Pulp Order, 1944. Dated July 12, 1944. Price 2d.

This Order re-enacts in substance the provisions of the Fruit Pulp (Control and Maximum Prices) Order, 1943. It also incorporates the provisions, hitherto contained in the Jam, Marmalade and Preserved Fruit (Licensing and Control) Order, 1941, prohibiting the manufacture of fruit pulp or fruit purée except under licence granted by the Minister.

The max. permitted quantity of added water per cwt. of fruit is 1½ galls. for cooked pulps (blackcurrant, redcurrant, whitecurrant, gooseberry, plum and apple), 1 gall. for strawberry raw pulp and none for raspberry, loganberry and blackberry. For all these the max. permitted quantity of preservative soln. is 3 pints per cwt. of fruit. Rhubarb and cherry are no longer included.

— **No. 841. The Preserves Order, 1944. Dated July 17, 1944.** Price (together with No. 842) 6d.

This is a consolidating Order, revoking and in substance repeating the provisions of the Mincemeat and Fruit Curd (Control and Maximum Prices) Order, 1941, as amended, the Honey (Maximum Prices) Order, 1942, the Honey (Control) Order, 1942, and the Jam and Marmalade (Control and Maximum Prices) Order, 1943, as amended.

The Order also revokes the Jam, Marmalade and Preserved Fruit (Licensing and Control) Order, 1941, as amended and repeats its provisions as regards jam and marmalade.

The labelling provisions have been altered to bring them into conformity with the Labelling of Food Order, 1944. The standards for jam, etc., are not repeated, but are prescribed under a separate Food Standards (Preserves) Order, 1944 (No. 842).

— **No. 842. The Food Standards (Preserves) Order, 1944. Dated July 17, 1944.**

This Order, which should be read with the Food Standards (General Provisions) Order, 1944, prescribes standards for jam, marmalade, fruit curd and mincemeat. The standards for jam, marmalade and fruit curd correspond to the provisions previously contained in the Jam and Marmalade (Control and Maximum Prices) Order, 1942, and the Mincemeat and Fruit Curd (Control and Maximum Prices) Order, 1941, except that an increased fruit content (30%) is prescribed for jams containing strawberries or gooseberries. A standard is now prescribed for mincemeat: *not less than* 65% *of soluble solids by refractometer.*

— **No. 850. The Soap (Licensing of Manufacturers and Rationing) Order, 1944. Dated July 18, 1944.** Price 3d.

This Order re-enacts the Soap (Licensing of Manufacturers and Rationing) Order, 1942, with minor amendments. In particular, it is provided that certificates of a Public Analyst or the Government Chemist shall prove themselves unless challenged.

The British Pharmacopoeia, 1932

We have been asked to draw attention to the following amendments.

The Schedule—Pulvis Ipecacuanhae et Opii—Potassium Sulphate of the British Pharmacopoeia, 1914, may be used, in place of Lactose, in making this preparation.

Pepsinum. Pancreatinum—Sucrose may be used, in place of Lactose, as diluent in making these preparations.

British Standards Institution

The following new standard has been issued.

B.S. 735—1944. British Standard Methods for the Sampling and Analysis of Coal and Coke for Performance and Efficiency Tests on Industrial Plant.*

The sampling and analysis of coal and coke for general industrial purposes have been dealt with in B.S. 1016—1942 and B.S. 1017—1942. The improved methods of analysis laid down in those Specifications have been substituted for those in B.S. 735—1937, which is now replaced by the present Standard.

Part I deals with Sampling, Part II with the Analysis of Coal Sample, and Part III with Analysis of Coke Sample. Experimental evidence on the Collection of Moisture Sample is summarised in Appendix B. Samples collected for determination of moisture as described in the Specification gave satisfactory results, but relatively large samples gave lower figures, indicating loss either in the handling, air-drying or crushing.

Appendix C describes and illustrates suitable forms of sample dividers.

* British Standards Institution, 28, Victoria Street, London, S.W.1. Price 5s. post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Nux Vomica in the Form of Powder. T. E. Wallis and J. W. Fairbairn (*J. Roy. Micros. Soc.*, 1943, **63**, 1–13)—A method based upon the determination of the total length of the linear fragments of the ribs of the epidermal trichomes per mg of the powdered drug is described. *General Method*—Place 0·1 g of powdered, air-dry nux vomica and 0·1 g of lycopodium on a glass plate, add 0·5 ml of alcohol (95%) and thoroughly mix. Gradually add 1 ml of a 1% soln. of safranin in 50% alcohol, leave for 10 min., add 1 ml of 10% hydrochloric acid to de-stain the non-lignified tissues, and dilute to 8 ml with a suspending agent consisting of 7 vols. of glycerin, 5 vols. of mucilage of tragacanth and 4 vols. of water. Transfer the suspension to a corked specimen tube, shake by gentle oscillation for 3 min. and prepare four slides by the method of Wallis ("*Practical Pharmacognosy*," 4th Ed., 1943, p. 185). Using a 4 mm. objective at *ca.* ×350, count the number of lycopodium spores and measure the length of each piece of rib, with the aid of a camera lucida, in each of 24 fields selected from each slide by the scheme of Wallis (ANALYST, 1935, **60**, 520). From the data obtained calculate the length of rib per mg of the powder (*i.e.*, per 94,000 lycopodium spores). The length of rib per mg of powdered seed was thus determined for 5 samples from different habitats and grown at different seasons. The average value obtained was 184 cm. per mg of air-dry seed with a variation from mean of ±10·5%. It is pointed out that this variation is due to habitat and season and it is of the same order of magnitud as that noted by Saber for senna leaves (*Quart. J. Pharm.*, 1934, **7**, 161) and for linseed (*id.*, 645), *viz.*, ±15%. The value obtained for one of the samples was confirmed by a geometrical method. The procedure was applied to the determination of powdered nux vomica in two typical veterinary medicines. Since these mixtures contained carbonates, a preliminary treatment with hydrochloric acid was included, and it was found that results were *ca.* 11% low. A redetermination of the standard figure for nux vomica, including the preliminary hydrochloric acid treatment, gave a value of 168 cm per mg, whence the proportions found in the two medicines were 17·36% and 29·81%, which were in good agreement with the amounts actually present, *viz.*, 17·65% and 30·00% respectively. It is stressed that whenever the general method is departed from a fresh standard figure should be determined. J. A.

Rapid and Simple Method for the Determination of Ephedrine. K. Schoen (*J. Amer. Pharm. Assoc.*, 1944, **33**, 116–118)—Difficulties inherent in the assay of ephedrine due to its solubility in water, its low m.p. and its volatility are overcome by steam-distilling the base quantitatively from a strongly alkaline solution. *Method*—Transfer an amount of the ephedrine preparation (in the form of soln., spray, syrup, jelly or tablet) expected to contain *ca.* 20–200 mg of base to the flask of a micro-Kjeldahl apparatus, add 10–15 ml of 50% sodium hydroxide soln. and distil in a rapid current of steam. Collect 50–150 ml of distillate, according to the amount of ephedrine present, in an excess of standard acid and back-titrate the excess with standard sodium hydroxide, using methyl red as indicator. The end-point is denoted by a salmon-pink colour. 1 ml of 0·1 *N* H_2SO_4 ≡ 0·01652 g of anhydrous ephedrine. The presence of ephedrine in the distillate was proved by isolating ephedrine hydrochloride according to the method of the U.S.P. XII and comparing its m.p. with that of an authentic sample; under these conditions, adrenaline is not volatile. Results are given for the application of the method to various preparations of ephedrine, recoveries being 99·2% to 99·9%.

Amphetamine—The same method can be applied to the assay of preparations of amphetamine (1-phenyl-2-amino-propane); the determination is much more rapid since this base is less soluble than ephedrine in water. 1 ml of 0·1 *N* H_2SO_4 ≡ 0·01351 g of amphetamine. J. A.

Assay of Pamaquin. C. W. Ballard and J. S. Pierce (*Quart. J. Pharm.*, 1944, **17**, 30–38)—The methods official in the 4th Addendum to the B.P. 1932 and in the U.S.P. XII are compared and criticised and improved procedures are described. *Moisture*—Drying at 100° C. for 6 hr. gives a value in close agreement with that given by the distillation method of Tate and Warren (ANALYST, 1936, **61**, 367) and is recommended.

6-Methoxy-8-aminoquinoline—The B.P. limit test for this impurity is shown to admit of the presence of up to 2·6%. Dissolve 0·1 g of pamaquin in 1 ml of 95% acetone, add 3 ml of 10% hydrochloric acid dropwise with shaking, then add 50 ml of water and filter. Wash the ppt. with 3 quantities each of 10 ml of hot water, neutralise the filtrate and washings with sodium hydroxide, add 0·5 *N* hydrochloric acid until the liquid is bright and dilute to 100 ml. To 10 ml add 1 ml of *N* hydrochloric acid, cool to 5° C., add 2 ml of 2·5% soln. of sodium nitrite at 5° C., mix well and leave for 5 min. at 5° C. Pour into a mixture of 2·5 ml of 10% soln. of sodium carbonate and 2·5 ml of a 0·16% soln. of disodium 2-naphthol-3 : 6-disulphonate in water, leave for 30 min. at 20° C. and measure the colour by means of a Lovibond Tintometer. A blank determination should be carried out by pouring the diazotised soln. into 5 ml of a 5% soln. of sodium carbonate; a difference of 1 red unit between the readings for the two solutions represents 0·052 mg of 6-methoxy-8-aminoquinoline. [*Abstractor's Note*: The size of the cell used is not stated; it would probably be 1 cm.]

Methylene-bis-β-hydroxynaphthoic acid—Dissolve *ca.* 0·75 g, accurately weighed, in 5 ml of acetone containing 5% of water, add 10 ml of 10% hydrochloric acid dropwise with stirring, and leave for 15 min. Dilute with 100 ml of water, allow the ppt. to settle, filter off through a tared sintered glass crucible, wash with 100 ml of 0·1 *N* hydrochloric acid at 60° C., and then with 10 ml of water, and dry to constant weight at 100–120° C.

Titratable bases as pamaquin base—Neutralise the filtrate and washings from the assay for methylene-bis-β-hydroxynaphthoic acid with 20% sodium hydroxide soln. and add 0·5 ml in excess. Extract with 50 ml, 25 ml, and 25 ml of ether, wash the combined extracts with 5-ml quantities of water until the washings are neutral to phenolphthalein, remove most of the ether, add 30 ml of 0·05 *N* hydrochloric acid and warm until complete solution is effected. Titrate with 0·05 *N* sodium hydroxide, using bromo-cresol purple as indicator: 1 ml of 0·05 *N* hydrochloric acid ≡ 0·01577 g of $C_{19}H_{29}N_3O$.

Total base—Proceed as in the determination of

titratable bases, but evaporate the ethereal extract to dryness with three 5-ml quantities of acetone, dry at 100° C. for 1 hr. and weigh. It is pointed out that the results obtained for the titratable bases are lower than that for total base in proportion to the amount of 6-methoxy-8-aminoquinoline present; this would have to be taken into account if a method involving titration were adopted. J. A.

Comparison of the Biological and Chemical Assays of *Atropa Belladonna* and *Atropa acuminata*. **J. A. Gunn** (*Quart. J. Pharm.*, 1944, **17**, 7–18)—The activities of liquid extracts of belladonna prepared from *Atropa Belladonna* and from *Atropa acuminata* (Indian belladonna) have been compared by measuring the degree of antagonism produced by the substance under test against the effect of a known amount of the parasympathetic stimulant carbachol on the isolated mammalian tissue. The results indicate that the alkaloids of *Atropa Belladonna* as determined by the method of the B.P. 1932 have three times the activity of the alkaloids of *Atropa acuminata* as determined by the same method, whereas the true hyoscyamine alkaloids of the two species as determined by the method proposed for the Seventh Addendum to the B.P. 1932, which excludes the volatile bases devoid of the characteristic actisuo of atropine, are identical in activity. Similar preparations made from the two species should, therefore, possess the same therapeutic activity provided that they are standardised by the method proposed for the Seventh Addendum to the B.P. It is further shown that the active alkaloids of *Atropa Belladonna* and of *Atropa acuminata* both possess *ca.* twice the activity of atropine sulphate. J. A.

Biochemical

Higher Fatty Aldehydes. II. Behaviour of the Aldehydes and their Derivatives in the Fuchsin Test. **M. Anchel and H. Waelsch** (*J. Biol. Chem.*, 1944, **152**, 501–509)—The method of Feulgen and Grünberg (*Z. physiol. Chem.*, 1938, **257**, 161) has been modified; the colour test is now carried out at 37° C. and the coloured product is extracted with capryl alcohol instead of with amyl alcohol. Synthetic palmitaldehyde and stearaldehyde acetals are recommended for use as standards. To an acetic acid soln. of the aldehyde in a glass-stoppered cylinder, add 3 drops of 6% mercuric chloride soln., 40 ml of fuchsin reagent* and 1 ml of *N* hydrochloric acid. Shake and place the tightly stoppered cylinders in a water-bath at 37° C. for 18 to 24 hr. Cool and extract the coloured products by shaking for ½ min. with 10 ml of capryl alcohol (purified by addition of sodium and subsequent distillation). Centrifuge the alcoholic solns., transfer to standard test-tubes and measure the colour in a photoelectric colorimeter with Corning filters 440 and 348. Either palmitaldehyde or stearaldehyde acetal can be used as a standard (both give identical readings), and a soln. in acetic acid is stable at room temp. for about 3 weeks. The method can be used for the estimation of higher fatty aldehydes in fatty animal tissues. Suspend a 1-g sample of minced muscle tissue in 10 ml of acetone, shake for 1 hr. at room temp., decant the liquid and repeat the extraction. Evaporate the acetone extract to dryness *in vacuo* and dissolve the residue in acetic acid. Extract a 100-mg sample of brain tissue or a 20-mg sample of nerve with two 5-ml portions of boiling 95% ethyl alcohol and then with ten 2-ml portions of boiling ether. Evaporate the combined extracts as before and dissolve the residue in acetic acid. F. A. R.

* Dissolve 1·0 g of fuchsin in 700 ml of boiling water, add 100 ml of *N* hydrochloric acid, cool to room temp. and add 5·00 g of anhydrous sodium bisulphite. Dilute to 1 litre and leave for 24 hr.

Estimation of Allantoin in Blood. **E. G. Young, C. C. MacPherson, H. P. Wentworth and W. W. Hawkins** (*J. Biol. Chem.*, 1944, **152**, 245–253)—The Rimini-Schryver reaction has been applied to the estimation of allantoin in blood. The method depends on the hydrolysis of allantoin to allantoic acid and then to glyoxylic acid, the latter being estimated by means of a colour reaction with phenylhydrazine and potassium ferricyanide. Difficulty was encountered in inducing phenylhydrazine to react with glyoxylic acid in preference to glucose, but this was overcome by hydrolysing allantoic acid with 0·02 *N* hydrochloric acid at 100° C. and causing the product to react with phenylhydrazine at 25–30° C. A second difficulty, removal of protein without undue dilution, was overcome by adopting anhydrous sodium sulphate as protein precipitant. Pipette 5 ml of oxalated whole blood into a 50 ml beaker, add 10 ml of water and warm to 40° C. Add 8 g of anhydrous sodium sulphate in small amounts at a time, with stirring, which is continued for a further 30 min. Filter as rapidly as possible through a Buchner funnel, keeping the mixture at 40° C. during filtration, and collect the filtrate in a glass tube, 1 × 3 in., with a small hole in the bottom plugged with a small piece of rubber. Immerse the filtrate in ice-water, stirring the mixture occasionally as $Na_2SO_4.10H_2O$ crystallises out. Remove the rubber plug, wipe the tube and put it into a 50-ml centrifuge tube. Centrifuge for 3–5 min. and then immerse the centrifuge tube in an ice-bath for 5 min. to ensure that no further crystallisation occurs. Pipette 1-ml portions of the soln. into small test-tubes graduated at 5 ml, add 0·1 ml of *N* sodium hydroxide soln., incubate at 37° C. for 12 hr., and add 0·15 ml of *N* hydrochloric acid. Pipette 1 ml of standard potassium allantoate (20 mg in 1 litre of 0·01 *N* sodium hydroxide soln. prepared every 3 months) into a similar tube and add 0·05 ml of *N* hydrochloric acid. Immerse the tubes in boiling water for *exactly* 2 min. and then transfer to an ice-water bath. To each tube add 0·2 ml of phenylhydrazine hydrochloride soln. (0·05 g in 15 ml of water prepared daily), mix and place in a bath at 30° C. for 15 min. Transfer to an ice-salt bath at −10° C. until incipient freezing occurs, and then add 0·6 ml of conc. hydrochloric acid cooled to −10° C. and 0·2 ml of potassium ferricyanide soln. (0·25 g in 15 ml of water prepared daily). Shake, leave for 30 mins. and then dilute to the mark with water and compare the colours in a Klett colorimeter. The concentration of allantoin (mg per 100 ml of blood) ≡

$$\frac{R_s}{R_u} \times C \times 0{\cdot}738 \times \frac{100}{v} \times \frac{d}{c}$$

where R_s represents reading of standard; R_u, reading of the unknown; C_s, mg of potassium allantoate in 1 ml of standard; v, vol. of filtrate used; 0·738, factor for converting allantoate to allantoin; d, degree of dilution; c, factor of concn. The degree of concentration (c) brought about by

the use of sodium sulphate was found experimentally to range from 2·1 to 2·5 according to the conditions; a ratio of 2·5 gives satisfactory results for most purposes. The visual colorimetric method is accurate to within ±10%; it cannot be used where the concentration of allantoin is very low; in such instances the use of a photo-colorimetric method is recommended Precipitate the protein in 1 ml of blood with sodium tungstate and sulphuric acid by the Folin-Wu method, shake and leave for 15 min. before filtration. Treat 1-ml portions of the centrifugate as described above, but make the final volume 5 ml instead of 3 ml. Measure the optical density, using a 530$m\mu$ Corning filter, and calculate the results from a standard curve prepared with pure allantoin. Recoveries of added allantoin were approximately quantitative.

E. A. R.

Reducing Substances in Urine. Improved Precipitating Agents. M. Dittebrandt, M. Tenney and E. S. West (*J. Biol. Chem.*, 1944, **152**, 395–400)—Urine filtrates prepared by the acid mercuric sulphate—barium carbonate technique of West and Peterson (*Biochem. J.*, 1942, **26**, 1720) give high values for fermentable sugar, owing to hydrolysis of some precursor of the sugar by the acid of the reagent. Improved methods now developed overcome this difficulty. In one method ferric sulphate, Lloyd's reagent and barium carbonate, and, in the other method ferric sulphate, Lloyd's reagent and lead carbonate are used. *Method I*—Add 10 ml of urine to 55 ml of water, followed by 15 ml of 20% ferric sulphate soln. and 4·0 g of Lloyd's reagent. Shake, leave for 3–4 min. and then add 35–40 g of solid barium carbonate with shaking until no more free carbon dioxide is evolved. Stopper the flask and shake vigorously, releasing the pressure from time to time. If the mixture is acid to litmus add a little more barium carbonate and repeat the shaking. Filter and acidify the filtrate to Congo red with a drop of sulphuric acid; filter off the barium sulphate. Ferment a portion of the filtrate with washed yeast and transfer aliquot portions of the fermented and unfermented filtrates into sugar tubes, neutralise to phenol red, and determine the reducing values with Shaffer-Somogyi reagent 50 (*J. Biol. Chem.*, 1933, **100**, 695) or with Somogyi's micro reagent (*J. Biol. Chem.*, 1937, **117**, 771). *Method II*—This is the same as Method I, except that the soln. is neutralised with 40 g of lead carbonate instead of with barium carbonate. After acidifying the filtrate with sulphuric acid remove traces of lead with hydrogen sulphide and then excess of the latter with a stream of moist air. Then proceed as described above. F. A. R.

Estimation of the Dicarboxylic Amino Acids in Protein Hydrolysates. R. K. Cannan (*J. Biol. Chem.*, 1944, **152**, 401–410)—A simplified method of separating acidic amino acids, which facilitates their subsequent estimation, has been based on adsorption of the acids from a protein hydrolysate by a basic resin, followed by elution with hydrochloric acid. The eluate contains no more than traces of amino acids other than dicarboxylic acids, and from it, glutamic acid hydrochloride and copper aspartate may be crystallised directly in pure form and more readily than from Foreman's fraction. In a protein hydrolysate, prepared with excess hydrochloric acid, the chief anions present are those of hydrochloric acid and the dicarboxylic amino acids, and these only should be adsorbed when the hydrolysate is treated with sufficient Amberlite IR–4 to raise the *p*H to 6 or 7. For the soln. to be electrically neutral,

$$a + c - b = (a + c)\alpha = a\alpha_a + c\alpha_c,$$

where a, b and c are the equivalents of acidic amino acids, bases and chloride respectively, α is the fraction of the total anions bound by the resin and α_a and α_c are the fractions of the total dicarboxylic amino acids and of chloride bound respectively. Where adsorption is determined solely by electrostatic forces, $\alpha = \alpha_a = \alpha_c$, so that substantially complete removal of the acidic amino acids by a single treatment with resin will occur only if hydrochloric acid is present in large excess or if the greater part of the bases is removed from soln. prior to treatment with resin. These conditions are employed in methods I and III respectively. In a third form of carrying out the estimation (Method II) treatment with the resin is repeated several times. It was established experimentally that Amberlite IR–4 exhibits a small but definite selective adsorption of chloride ions relative to the mono-anions of glutamic and aspartic acids, but that the difference between α and α_a was too small to invalidate the general conclusions stated above. *Method I*—Hydrolyse the protein by boiling with 6 *M* hydrochloric acid (50*mM* per g of protein) for 24–30 hr. Dilute to 50 ml, filter off insol. humin, and neutralise the filtrate and washings by stirring for 1–3 hr. with *ca.* 50 g of the (moist) resin per g of protein (the resin should first be washed with liberal amounts of 4% hydrochloric acid, water, 4% sodium hydroxide soln. and water, and the cycle of operations repeated several times). Decant the soln. from the resin and wash the latter repeatedly by decantation. Filter and acidify the combined filtrates and washings with hydrochloric acid (10*mM* per g of protein), neutralise with fresh resin, filter and wash as before. Repeat the process once more, increasing the time of adsorption to compensate for the increased dilution. Extract the resin repeatedly with 0·25*M* hydrochloric acid until the *p*H of the extract falls below 2; about 10 ml of acid are required per g of resin. Concentrate the combined extracts and washings to about 20 ml *in vacuo*, decolorise with a little Norit, and evaporate the soln. to dryness; use the residue for analysis. *Method II*—Remove free hydrochloric acid from the hydrolysate by repeated distillation to a syrup, dissolve the syrup in water, filter off humin and neutralise with about 10 g of resin per g of protein. Re-acidify the filtrate and washings and treat again as in Method I, repeating the adsorption 3 or 4 times. Extract the resin as described in Method I. *Method III*—Dilute the hydrolysate, if necessary, and add a slight excess of 30% phosphotungstic acid soln., heat the soln. to 90° C. and leave to crystallise overnight. Filter off the ppt. and, without washing, suspend it in hot water containing 1% of phosphotungstic acid and 0·25*M* of hydrochloric acid. Again crystallise, filter off and wash the ppt., and concentrate the combined filtrates from both pptns. and the washings to a small vol. *in vacuo*. Remove the excess of phosphotungstic acid with amyl alcohol and ether and the free hydrochloric acid by distillation to dryness *in vacuo*. Dissolve the residue in water and treat as described in Method II, using 2 or 3 adsorption cycles. The advantage of method III is that cleaner extracts are obtained than by the other methods. All three methods give substantially the same result, with recoveries better than those obtained by Calvery

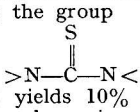
(*J. Biol. Chem.*, 1931–32, **94**, 613), but less than those obtained by Chibnall *et al.* (*Biochem. J.*, 1943, **37**, 372; Abst., ANALYST, 1944, **69**, 56). The slightly lower results are compensated for by the greater simplicity of the method. F. A. R.

Estimation of the Dicarboxylic Amino Acids by Titration. A. C. Kibrick (*J. Biol. Chem.*, 1944, **152**, 411–418)—The method of Cannan (*cf.* preceding abstract), although simpler than that used by Chibnall *et al.* (*Biochem. J.*, 1943, **37**, 372; Abst., ANALYST, 1944, **69**, 56), is too tedious for routine work and a still simpler method has now been devised. Although ninhydrin cannot be used for the estimation of total dicarboxylic amino acids, it can be used for aspartic acid, since it reacts with both carboxy groups. If g, a and n, represent the moles of glutamic, aspartic and non-acidic amino acids respectively then (I) Total COOH groups $= 2g + 2a + n$. (II) Ninhydrin-reactive groups $= g + 2a + n$. (III) Formaldehyde-reactive N atoms $= g + a + n$, and it is evident that by estimating these three values the individual as well as the total dicarboxylic acids can be calculated. Possible sources of error are the presence of lysine or ammonia, which would lead to low values for aspartic acid, and of non-nitrogenous acids, such as phosphoric acid, which would increase the value for glutamic acid. Another disadvantage is that the method depends on measuring differences between amounts of the same order of magnitude. Hydrolyse the protein with hydrochloric acid and remove excess by distillation *in vacuo*. Dissolve the residue in water and adsorb with Amberlite IR–4 by one or other of Cannan's methods. Evaporate the hydrochloric acid eluate *in vacuo* and dissolve the residue in water to give a soln. with *p*H slightly below 2. Determine carboxyl groups in a part of this soln. by the ninhydrin method; to the remainder add sufficient potassium chloride to make the soln. about 0·3 *M* when diluted to 25 ml, and titrate with 0·25 *M* sodium hydroxide soln. to *p*H 7, using a glass electrode. Add sufficient neutral formaldehyde soln. (prepared by treating the commercial soln. with the basic form of Amberlite IR–4) to give a concn. of about 8%, and continue the titration to *p*H 9·5. Titrate the same conc. of formaldehyde in 0·3 *M* potassium chloride soln. and subtract the titre from the value found in the main formaldehyde titration; the result gives the equiv. of formaldehyde-reactive nitrogen. Similarly apply to the titration in water from *p*H 2 to 7 a correction for the acidity of dilute solns. of hydrochloric acid in 0·3 *M* potassium chloride soln. The method gives values for both glutamic and aspartic acids in substantial agreement with those obtained by Chibnall *et al.* Two adsorption cycles were found sufficient with Cannan's Methods I or III, but Method II proved to be much less efficient, and is not recommended; Method III is preferred for routine use, as it requires less resin. F. A. R.

Determination of Thiourea. L. C. Chesley (*J. Biol. Chem.*, 1944, **152**, 571–578)—The method suggested is based on that of Grote (*J. Biol. Chem.*, 1931, **93**, 25) in which sodium nitroferricyanide is allowed to stand in an alkaline medium whereby it is converted into an unidentified substance which reacts with thiourea to give first a blue, then a purple-red and finally a crimson colour. In estimating the thiourea content of serum or plasma, shake 1 vol. with an equal vol. of 2/3 *N* tungstic acid soln. and then filter or centrifuge. With urine, simply dilute with water to give a concn. of 2 to 10 g of thiourea per ml. Pipette 3 ml of serum filtrate or diluted urine into a colorimeter tube, and add 3 ml of the diluted colour reagent, prepared as follows. Pipette 10 ml of 5% sodium nitroferricyanide soln. into a 50-ml flask, and add 5 ml of 10% hydroxylamine hydrochloride. Mix and, after exactly 2 min., add 10 ml of 10% sodium bicarbonate soln.; again mix, and after exactly 10 min. add 0·11 ml of bromine. Again mix and after a further 10 min. add 5 ml of 2% phenol soln. After 10 min. dilute a portion of this stock soln. 20-fold with 0·05 *M* phosphate buffer soln. at *p*H 6·0. Treat appropriate serum and urine blanks in the same way. Measure the colours in an Evelyn photoelectric colorimeter with a filter having max. transmission at 580$m\mu$, taking readings at 10-min. intervals until these are constant and minimal. The time for full colour development varies, but is usually 50 to 70 min. with serum and 20 to 40 min. with urine. The error of single determinations was less than 2%. F. A. R.

Methods for the Determination of Thiouracil in Tissues and Body Fluids. R. H. Williams, B. J. Jandorf and G. A. Kay (*J. Lab. Clin. Med.*, 1944, **29**, 329–336)—Grote (*J. Biol. Chem.*, 1931, **93**, 25; Abst., ANALYST, 1931, **56**, 760) found that certain organic sulphur compounds gave a blue colour when treated with a reagent made by the action of hydroxylamine hydrochloride and bromine on sodium nitroprusside in sodium bicarbonate soln. A method for the determination of thiouracil (2-thio-6-oxypyrimidine) based on this reaction is described. *Reagent*—Dissolve 0·5 g of sodium nitroprusside in 10 ml of water without heat, add 0·5 g of hydroxylamine hydrochloride followed by 1 g of finely-powdered sodium bicarbonate and keep covered with a watch-glass until effervescence ceases. Add 0·1 ml of bromine and again leave until gas is no longer evolved. Filter the mahogany-brown soln. and dilute to 25 ml. The reagent should be diluted a further five-fold before use. *Standard Curve*—Adjust the *p*H of a soln. of thiouracil in water containing 10 mg per 100 ml to 8·5 with *N* sodium hydroxide, using a glass electrode. To a number of tubes add aliquot portions of 0·05 to 1 ml and dilute with water to 1 ml. To each add 1 ml of Grote's reagent, leave for 15 min., add 4 ml of 1% sodium chloride soln. and immediately measure the intensity of the greenish-blue colour, *e.g.*, in an Evelyn photoelectric colorimeter with a 660 filter and a No. 6 diaphragm. Use a mixture of 1 ml of Grote's reagent and 5 ml of 1% sodium chloride soln. as a blank. When the results are plotted on semilogarithmic paper, a straight line is obtained. *Urine*—Adjust the *p*H of a specimen, preserved with chloroform or hydrochloric acid, to 8·5 with *N* sodium hydroxide. Centrifuge about 10 ml, transfer 0·25–0·5 ml to a tube, add 1 ml of Grote's reagent, leave for 15 min., dilute to 6 ml with 1% sodium chloride solution and measure the colour. *Blood*—Add 1 ml of water to 1 ml of oxalated blood, adjust the *p*H to between 8·0 and 8·5, add 0·1 ml of a 5% soln. of trypsin (tech.) and incubate the mixture at 37° C. for 12 hr. Prepare a protein-free filtrate using 1 ml of the digested blood mixture, 7 ml of water, 1 ml of 5% copper sulphate soln. and 1 ml of 7% sodium tungstate soln. and adjust the *p*H to between 8·5 and 9·0. Add 1 ml of Grote's reagent to 5 ml of the filtrate, filter through a Whatman No. 2 paper if a slight cloudiness should develop, leave for 15 min. and

measure the colour. *Tissues*—Add an equal vol. of water to the tissue and *ca.* half this vol. of *N* sodium hydroxide, triturate until a homogeneous suspension is produced and leave overnight in an ice-box. Prepare a protein-free filtrate with 1 ml of the mixture and continue as described for blood. With liver it is advisable to remove the excess of fat by extraction of a weakly alkaline suspension of the tissue with ether before continuing the determination. The undiluted reagent is stable for at least 2 weeks if kept in an ice-box, but it is advisable to test it with standard thiouracil soln. at the end of that period. The colour developed in a test after *ca.* 15 min. at room temp. is a maximum, appreciable fading taking place if the mixture is left much longer. After dilution to 6 ml, however, the decrease in colour is only 3% on standing for 1 hr. Light affects the reaction, only 40% of the maximum intensity developing after 15 min. in the dark. It is claimed that under the conditions described, the reaction is limited to those compounds possessing the group



sodium pentothal yields 10% and thiobarbituric acid 35% of the colour given by an equivalent amount of thiouracil. Thiourea gives an intense blue colour with the reagent. The two tables of results indicate that good recoveries are obtained.

J. A.

Relation of the Concentration of Vitamin A, Carotenoids and Cholesterol in Milk Fat to the Size of the Fat Globules. S. K. Kon, E. H. Mawson and S. Y. Thompson (*Nature*, 1944, **154**, 82)—In measuring the vitamin A and carotene content of samples of fat churned or extracted by solvents from the same batch of milk, Henry, Kon, Gillam and White (*J. Dairy Res.*, 1939, **10**, 114) found that while the concn. of vitamin A was the same for both methods of preparation, there was slightly more carotene in the *extracted* fats, and this they attributed to loss on churning. This is now shown to be incorrect, the difference being due to the relatively high carotene content of the small amount of residual fat in the separated milk. Vitamin A and carotenoids have been determined at the different stages of butter making and specimen results are as follows:

Fraction	Method of extraction of fat	Fat g per 100 ml	Carotenoids μg per g fat[3]	Cholesterol mg per g fat	Vitamin A I.U. per g fat	Iodine value of fatty acids	Av. radius of fat globules; mean of 200 measurements μm
Milk	Solvent[1]	3·14	9·8	3·3	24·7	38·5	1·41
Cream	Solvent[1]	35·35	9·5	2·8	25·3	41·5	1·68
Separated milk ..	Solvent[1]	0·06	65·4	36·0	21·6	45·2	0·51[4]
Butter	Churning[2]	86·90[2]	9·4	2·5	26·3	40·2	—
Buttermilk ..	Solvent[1]	1·98	12·2	6·0	24·2	42·3	0·89
Whey	Solvent[1]	0·42	14·9	5·6	23·2	37·8	1·09
Whey cream ..	Solvent[1]	18·20	9·4	3·3	24·7	40·2	1·80
Separated whey ..	Solvent[1]	0·03	11·0	46·0	26·2	48·0	[5]
Whey butter ..	Churning[2]	83·90	9·3	2·7	26·3	40·1	—
Whey buttermilk ..	Solvent[1]	2·25	12·4	5·3	23·9	42·0	0·84

[1] Method of Olson, Hegsted and Peterson (*J. Dairy Sci.*, 1939, **22**, 63) slightly modified.
[2] g per 100 g.
[3] The amount of carotene measured chromatographically varied little in the different fat fractions; the range was 74–83%.
[4] Only 50 globules measured.
[5] Owing to the small size and scarcity of the globules, no satisfactory measurement was possible.

The difference in distribution between vitamin A and carotenoids is emphasised. The concns. of carotenoids and cholesterol are very much higher in the smaller milk fat globules than in the larger globules, but the concn. of vitamin A is about the same in both. It is suggested that the figures indicate that the vitamin is in true solution in the oil, while the carotenoids and cholesterol may be associated in some way with the fat globule membrane. J. A.

The Antimony Trichloride Method for Determination of Vitamin A. G. H. Benham (*Canad. J. Research*, 1944, Sec. B, **22**, 21–31)—Published information concerning the antimony trichloride method of vitamin A determination is summarised and reviewed. Recommendations about several details of technique are made, and results are given of expts. made to resolve some of the divergences between published methods. Careful precautions are necessary in extracting the unsaponifiable part of the sample and in washing and drying the extract, or losses of up to 25% of the vitamin may occur. Faulty technique is more likely to give low results than decomposition during sampling, saponification and development of the blue colour. Final quantitative correlation between the chemical and biological methods must await synthesis of pure vitamin A and further study of the biological assay with regard to the effects of the diluting medium and the balance between vitamin A and other vitamins. For the purpose of the work reported, which is concerned only with the unsaponifiable fractions of the samples, the factor connecting extinction coefficient and vitamin A potency is taken as 2,700. *Summary of Recommendations*: *Storage of material*—It is desirable to work on fresh material to avoid changes by autoxidation. *Saponification*—Use the smallest possible excess of potash. Greater excess does not destroy vitamin but leads to emulsification and entails extra washing of the solvent extract. Regard saponification as complete when the soln. is homogeneous, *e.g.*, in 5 min. for 500 mg of fish oil or 20 ml of milk or colostrum, 30–45 min. for 5 g of liver. Correct dilution of the soap soln. with water is necessary to avoid later emulsification. [No definite dilution is suggested, but a table of data shows good results with 2, 3 or 4 vols. of water—resulting respectively in alcohol concentrations of

26%, 19% and 16%—when the subsequent extraction is with ether—Abstractor.] *Solvent extraction*—Use ethyl ether, 3 extractions being sufficient. No emulsification occurs unless too much potash was used and no addition of alcohol is needed. Light petroleum gives much lower and more erratic results than ether under the same conditions. *Washing of the extract*—Use 100 ml of water without shaking, 10 ml of water with shaking, 10 ml of $N/6$ potassium hydroxide with shaking, and water until the rinse shows no cloudiness with 10% hydrochloric acid. Some emulsion may form when the potash is used, and none must be lost with the washings. *Drying*—Dry the ethereal soln. *over* anhyd. sodium sulphate, decant into a graduated flask, adjust to the desired volume and add more sodium sulphate. Passage of the soln. *through* sodium sulphate is not favoured. *Light*—It is not necessary to work in subdued light or to use opaque apparatus. *Antimony trichloride reagent*—A soln., saturated at room temp., in chloroform, is used. The actual concn. is considerably affected by the alcohol content of the chloroform. *Development of blue colour*—Pipette 1 ml of dry ether soln. into an Evelyn colorimeter tube and evaporate the solvent by suction at a temp. below 40° C. Dissolve the residue in 1 ml of dry chloroform and place the tube in the colorimeter with a No. 620 filter in position. Add 9 ml of antimony trichloride reagent quickly and take the instrument reading. With the saturated reagent soln., the colour persists long enough for easy reading. L. A. D.

Determination of Vitamin B_1 in Urine. F. Urban and M. L. Goldman (*J. Biol. Chem.*, 1944, **152**, 329–337)—The method now proposed depends on the conversion of vitamin B_1 into thiochrome by means of sodium hydroxide and potassium ferricyanide, but the concn. of thiochrome is measured, not fluorometrically, but by the amount of light absorbed at its strong absorption band, 368$m\mu$. The 365$m\mu$ line of the mercury vapour arc is used for this purpose. The method is claimed to be more sensitive and reliable than the fluorometric method. To allow for the presence of impurities also absorbing at this wavelength, a blank estimation is carried out after treatment with benzene sulphonyl chloride which completely inhibits the conversion of vitamin B_1 into thiochrome. To 30 ml of a 24-hr. sample of urine, collected with 10 ml of glacial acetic acid, add 30 ml of *iso*butyl alcohol, shake for 1 min., centrifuge and discard the *iso*butyl alcohol layer. Filter the extracted urine and add 2 ml of glacial acetic acid and 8 ml of water to 20 ml of the filtrate. Activate a column of Decalso (5 to 7 g) by washing 50 times with boiling water and then with 2% acetic acid until the filtrate has *p*H 3·5, and run the urine through the column. Wash with three successive 10-ml portions of 2% acetic acid; this results in a loss of 10% of the adsorbed vitamin B_1. Elute the column with three 10-ml portions of 25% potassium chloride soln., and to 10 ml of the eluate add 3 ml of 20% sodium hydroxide soln. and then, after 3 min. shaking, 2 ml of freshly prepared 2% potassium ferricyanide soln. After *exactly* 1 min. add 12 ml of *iso*butyl alcohol, shake for *exactly* 2 min., centrifuge and dry the *iso*butyl alcohol extract. To a second 10-ml portion of the eluate add 3 ml of 20% sodium hydroxide soln. followed immediately by one drop of benzene sulphonyl chloride. After 3 min. shaking add 2 ml of potassium ferricyanide soln. and then, after *exactly* 1 min., 12 ml of *iso*butyl alcohol. Shake as before and dry the extract. Measure the extinctions of both butyl alcohol extracts and deduct that of the blank from that of the thiochrome soln. Calculate the thiochrome conc. from a calibration curve prepared from a soln. of crystalline vitamin B_1 (10–30μg in 5 ml) in the same manner. The recovery of vitamin B_1 added to urine was 89 ±5% with quantities ranging from 0·15 to 5μg per ml of urine. Allowing for the loss on washing the Decalso adsorbate with acetic acid, therefore, the recovery is quantitative. F. A. R.

Determination of Dehydroascorbic Acid and Ascorbic Acid in Plant Tissues by the 2 : 4-Dinitrophenylhydrazine Method. J. H. Roe and M. J. Oesterling (*J. Biol. Chem.*, 1944, **152**, 511–517)—Dehydroascorbic acid can be estimated in presence of ascorbic acid by adding thiourea to stabilise the ascorbic acid and then converting into the bis-2,4-dinitrophenylhydrazone, treating with sulphuric acid and measuring the resulting red colour photometrically. Grind the tissue under 20 to 50 parts of a soln. containing 5% of metaphosphoric acid and 1% of thiourea, filter and transfer 4 ml of the extract to each of three matched photoelectric colorimeter tubes, one of which is used as a blank. To each of the others add 1 ml of a 2% soln. of dinitrophenylhydrazine in 9 N sulphuric acid and incubate at 37° C. for 3 hr. Cool all three tubes in ice-water and while they are still at 0° C. add to each 5 ml of 85% sulphuric acid, one drop at a time, during not less than 1 min., and finally add 1 ml of dinitrophenylhydrazine soln. to the blank tube. Remove the tubes from the bath and after 30 min. measure the colour in a photoelectric colorimeter with a 540$m\mu$ filter. Calculate the results by treating a standard soln. in the same way or from a calibration curve made with standard solns. of dehydroascorbic acid in concns. ranging from 0·25 to 15μg per ml. To prepare the standard dehydroascorbic acid solns., treat a soln. of 25 mg of ascorbic acid in 25 ml of 5% metaphosphoric acid soln., with one or two drops of bromine. Shake until yellow, decant from the excess of bromine, and aerate until colourless. Make appropriate dilutions with 5% metaphosphoric acid soln. containing 1% of thiourea. Recoveries were slightly in excess of the theoretical. F. A. R.

Interference of Sesame Oil, Fish Oil, and Cholesterol with the Polarographic Determination of α-Tocopherol. J. J. Beaver and H. Kaunitz (*J. Biol. Chem.*, 1944, **152**, 363–365)—Smith, Spillane and Kolthoff (*J. Amer. Chem. Soc.*, 1942, **64**, 447) used the polarograph for estimating α-tocopherol in 75% alcohol in presence of an acetate buffer. Under these conditions the half-wave potential was +0·25 volt at 31° C. and the diffusion current was proportional to the concn. of tocopherol. Since fats and cholesterol are frequently associated with vitamin E, the effect of such substances on the polarographic determination of tocopherol was investigated. Fats in concns. of 2% were insoluble in an acetate buffer and in a citrate buffer of *p*H 4·6 when 75% alcohol was used as solvent. Attempts to obtain polarographic curves by emulsifying the fats failed. When 2·25 ml of a buffer soln., containing 0·025 M sodium benzoate and 0·025 M benzoic acid in 20 ml of acetone and 80 ml of water, were mixed with 5 ml of fat and 92·75 ml of acetone a clear soln. was obtained, but the currents obtained with the polarograph were only 0·1% of

those found with the acetate buffer in 75% alcohol. This made the quantitative determination of α-tocopherol extremely inaccurate. Sesame oil exerts a depressing effect on the current proportional to its concentration. Fish oil has a similar effect, and the influence of cholesterol is even more pronounced.
F. A. R.

Agricultural

Rapid Digestion Method for Determination of Phosphorus. D. W. Bolin and O. E. Stamberg (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 345)—Presence of molybdenum markedly increases the rate of oxidation of organic matter by a mixture of sulphuric and perchloric acids, and the use of this catalyst does not interfere with the quantitative colorimetric estimation of phosphorus. To prepare the digestion mixture, dissolve 30 g of sodium molybdate in 150 ml of water, slowly add 150 ml of conc. sulphuric acid and, when the mixture is cold, add 200 ml of 70–72% perchloric acid. Heat not more than 500 mg of the sample and a few glass beads in a 100-ml Kjeldahl flask with 5 ml of the digestion mixture over a micro burner until oxidation begins (1–2 min.). Remove the burner and allow digestion to proceed. Finally add 2 ml of perchloric acid, replace the burner and heat until the soln. is clear and free from charred matter (*ca.* 4 min.). Dilute the soln. to 100 ml, allow silica to settle, filter if necessary, and take a suitable aliquot portion for the colorimetric estimation, adjusting the acidity with perchloric acid to the approx. range of acidity (usually a wide one) stated in the method used. Two different colorimetric methods were used in the investigation, *viz.*, the formation of a blue colour by reduction of the phosphomolybdate (Sherman, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 182) and the formation of yellow phosphovanadiomolybdate (Koenig and Johnson, *Id.*, 1942, **14**, 155). A Cenco photelometer was used with a 420$m\mu$ filter for the yellow colour and a 600$m\mu$ filter for the blue colour and a reagent blank as reference liquid. The standard curve was made by plotting known amounts of phosphorus against the corresponding photelometer readings on semilogarithmic paper. For a suitable range of phosphorus content the Kjeldahl digestion flask may be calibrated and the reagents added directly. By the phosphovanadiomolybdate method phosphorus in samples containing 0·05–0·5% may be determined directly without further dilution. For material containing less than 0·1% of phosphorus and with a 500 mg sample the reduced phosphomolybdate method is the more suitable; for material containing higher amounts the vanadate method gives greater stability of colour. With samples of 500 mg or less the digestion proceeded smoothly and no explosions occurred. When compared with the ashing method the variation range of the rapid digestion method applied to typical samples of feeding stuffs ranged from −3·3 to +5·3%.
A. O. J.

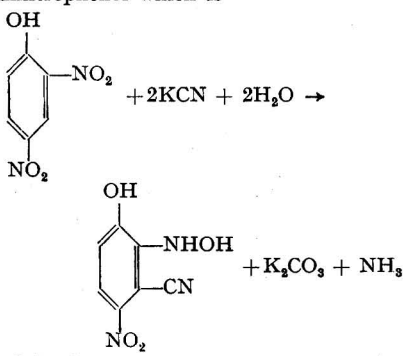
Organic

Furfural Determination. Iodine Method for Hydrolysed Wood Liquors. H. R. Rogers (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 319–321)—The following method gives accurate results with aq. solns. of pure furfural. In presence of other substances reacting with iodine slightly high results are obtained, but the precision is sufficient when rapidity is desired for control purposes. The method was devised for aq. furfural solns. derived from hydrolysed wood liquors containing lower boiling constitutents ("heads"). In the blank reaction iodine reacts preferentially with the heads or lower alcohols, aldehydes, etc., but with only 12·5% of the furfural present, which is oxidised to furoic acid. In the sample reaction iodine reacts with all the furfural and with the heads and thus the total furfural can be calculated. The oxidation of furfural to furoic acid by iodine is a function of the alkalinity of the mixture, and not more than *ca.* 100 mg of pure furfural can be oxidised quantitatively, owing to the rapid formation of iodate and iodide before the original hypoiodite has reacted with all the furfural. To each of two aliquot portions of distillate containing 10–40 mg of furfural in 250-ml Erlenmeyer flasks add 4 or 5 drops of phenol red and make one portion (the blank portion) exactly neutral and the other approximately so. To the blank portion add 2 ml of *N* sodium hydroxide and, with swirling, 10 ml of 0·1 *N* iodine. Adjust the vol. to *ca.* 60 ml and leave at room temp. for 18–20 min. To the other portion add 10 ml of *ca.* 6 *N* sodium hydroxide followed by 10 ml of 0·1 *N* iodine. Adjust the vol. to 60 ml (*i.e.*, 1 *N*) and leave at room temp. for 10–12 min. To the blank portion add *ca.* 0·5 ml of 6·5 *N* sulphuric acid and titrate the excess of iodine (released from iodate and iodide) with 0·1 *N* sodium thiosulphate (B ml), using starch as indicator. To the other portion add an excess (*ca.* 10 ml) of 6·5 *N* sulphuric acid and titrate the liberated iodine as before (S ml). Then B–S is the amount of 0·1 *N* iodine required to oxidise 87·5% of the furfural present to furoic acid, and the amount of furfural (g) in the aliquot portion taken is $\frac{(B-S) \times N \times 0{\cdot}048}{0{\cdot}875}$, where N is the normality of the sodium thiosulphate soln. It is probable that iodine reacts with methyl furfural as well as with furfural. To adapt the method to the determination of xylose, the Tollens distillation method must be modified. In a litre flask fitted with a dropping funnel and connected through a Clark distilling head with a condenser, distil 0·6–1 g of xylose with 250 ml of 12% hydrochloric acid at the rate of 50 ml per 20 min., adding 12% hydrochloric acid through the funnel at the same rate. Make up the 450 ml of distillate collected in 3 hr. to 500 ml and take 25-ml aliquot portions for the method described. With 0·6–1·0 g of xylose use the divisor 0·54 to convert the furfural found into xylose instead of the Tollens divisor of 0·57.
A. O. J.

Analysis of *n*-Butane-*iso*Butane Mixtures by the Density Method. E. Solomon (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 348)—The method is similar to that of Leighton and Heldman (*J. Amer. Chem. Soc.*, 1943, **65**, 2276). The butane sample, which has been freed from olefines and from lighter and heavier hydrocarbons, is condensed into the inner chamber of a triple-walled Dewar flask. The middle chamber, containing liquid propane, is surrounded by an outer evacuated chamber and is further insulated with aluminium foil with appropriately placed windows. The temp. of the butane sample is adjusted by regulating the pressure over the boiling propane until a small glass float of appropriate density neither rises nor sinks. This pressure is rapidly adjusted either by applying a pressure of nitrogen or by evacuating with a water aspirator through a ballast volume. A small nichrome heating coil immersed in the propane

assists in the rapid attainment of the desired equilibrium temp., and a reflux condenser returns vaporised propane to the middle chamber. Since the relationships between *iso*butane concn. and either propane pressure or sample temp. (expressed as millivolts measured on a multijunction thermocouple immersed in the liquid) are not quite linear, it is necessary to construct calibration curves with a few known mixtures of *n*- and *iso*butane. The method can then yield results accurate to ±1% in 15–20 min. The sample can conveniently be *ca.* 10 ml or even less. A. O. J.

Colorimetric Determination of 2,4-Dinitroanisole. M. S. Schechter and H. L. Haller (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 325–326)—A yellow colour due to pyrethrum oleoresin and other substances in some insecticides containing 2,4-dinitroanisole prevents the use of the yellow colour of 2,4-dinitrophenol as the basis of a colorimetric estimation, but the purpuric acid reaction with potassium cyanide may be used. By analogy the reaction is presumed to be similar to that with 2,4-dinitrophenol which is

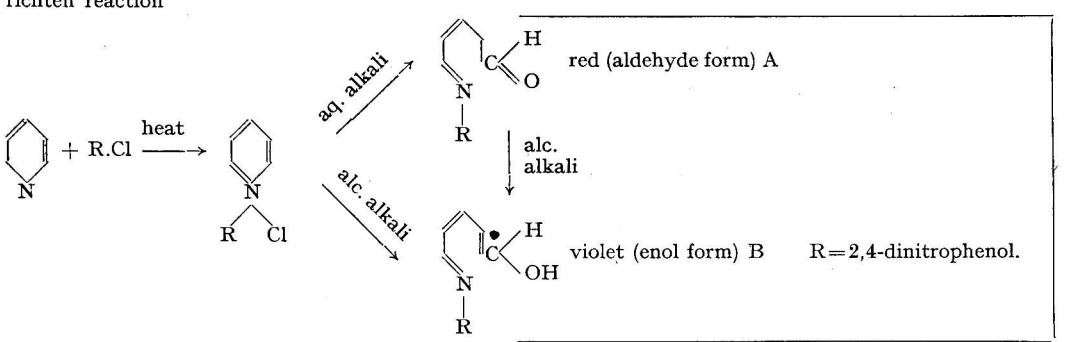


The following procedure was developed for an insecticidal dust containing 2% of 2,4-dinitroanisole, 2% of *N-iso*butyl undecylenamide, pyrethrum oleoresin (≡0·2% of total pyrethrum) and 1% of an antioxidant with pyrophyllite as diluent. Stir 2 g of the sample with 4 or 5 portions of acetone, decanting each portion through a Gooch crucible containing an asbestos mat and held in an all-glass Gooch funnel. Continue to wash with acetone until the filtrate measures 100 ml. Take a 10-ml and a 15-ml portion of the clear liquid and add 5 ml of acetone to the 10-ml portion. Prepare comparison standards containing 2, 4 and 6 mg of pure 2,4-dinitroanisole and dilute each to 15 ml with acetone. Add 5 ml of 0·5% aq. potassium cyanide soln. to each of the solns., mix and, after 1 hr., measure the colour in a photometer, using acetone as the blank soln. An Aminco photometer type F with a No. 58 yellow filter (max. transmission at *ca.* 580mμ) is recommended. Plot the results on semilogarithmic paper as % transmission (logarithmic ordinate) against concn. of 2,4-dinitroanisole. The concn. of the unknown soln. may then be read from the graph, which is linear in accordance with Beer's law. Samples said to contain 2% of 2,4-dinitroanisole with the other constituents already mentioned gave as the average of 10 determinations 2·17% (average deviation 0·05, max. deviation 0·12) with 10 ml aliquot portions and 2·11% (aver. deviation 0·04, max. deviation 0·11) with 15-ml portions. With samples containing much less than 2% of 2,4-dinitroanisole a more sensitive colour reaction may be used. Shake 25 ml of an acetone extract with 5 ml of *ca.* 35% sodium hydroxide soln. and leave for 30 min. A violet colour develops in the acetone layer. Decant the acetone layer into a photometer tube and measure the colour, using a No. 58 filter as before. The test is subject to interference and is too sensitive for use with samples containing *ca.* 2% of 2,4-dinitroanisole. Contamination with sulphur, even from rubber stoppers, must be avoided. 1-Chloro-2, 4-dinitrobenzene gives both the colour reactions described (*cf.* abstract on p. 283). A. O. J.

Phenyl *iso*Cyanate Derivatives of certain Alkylated Phenols. Melting Point and X-Ray Diffraction Data. J. B. McKinley, J. E. Nickels and S. S. Sidhu (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 304–308)—For the identification of the alkylated phenols used in the preparation of plastics, synthetic rubber, germicides, fungicides, etc., the m.p. of the aryl N-phenylcarbamate formed by reaction of the phenol with phenyl *iso*cyanate may be determined. The derivatives of a large number of phenols were prepared, and their m.p. and X-ray diffraction patterns were determined. Either will usually serve to identify the phenol, but a consideration of both gives unequivocal results. To prepare the derivatives, a method based upon the procedures of Steinkopf and Höpner (*J. prakt. Chem.*, 1926, **113**, 137) and Weehuizen (*Rec. trav. chim. Pays-Bas.*, 1918, **37**, 266) was used. Mix the phenolic substance (*ca.* 1 g) with a slight molar excess of phenyl *iso*cyanate in an 8-in. test-tube fitted with a reflux condenser, to the mixture add 8–10 ml of a petroleum distillate (170°–200° C.) fractionated from kerosene, and heat for 1–4 (usually 4) hr. Collect on a filter the crystals separating from the cold mixture and after recrystallisation from light petroleum, benzene or a mixture of these solvents and drying at room temp. determine the m.p. To obtain the X-ray diffraction pattern by the usual Debye–Scherrer–Hull method, pack a small portion of the finely powdered derivative into a short length of 19-gauge stainless steel hypodermic needle tubing (0·7 mm internal diam.), compressing with a plunger and finally extruding a portion of the material as a cylinder. Mount the steel tube in a camera of 57·3 mm effective diam., so that only the extruded portion of the specimen appears in the X-ray beam and photograph with filtered CuKα radiation having an effective wavelength of 0·1539mμ. A camera of 171·9 mm effective diam. gave better results with some samples. Generally the diffraction patterns are sharply defined. In the few instances in which diffraction lines representing different interplanar spacings merge, the merged lines may be considered as a group and measured as a single line, the spacing calculated from such measurement representing the shortest interplanar spacing of the group considered. Certain flaky substances tend to pack anisotropically causing preferred orientation of the crystallites in the extruded specimen. Since it is essential that the powdered specimen for a Debye–Scherrer–Hull diffraction photogram contain crystallites randomly oriented, diffraction data were obtained by using a rotating powdered sample loosely packed in a thin-walled Nylon tube. No evidence of preferred orientation of crystallites was found. Most of the phenols studied were of the alkylated type in which the alkyl groups were methyl, ethyl, *iso*propyl, *tert.*-butyl and *tert.*-amyl. Phenols that would not form aryl N-phenylcarbamates by reaction with phenyl *iso*cyanate were of the type in which both positions ortho to the

hydroxyl group were occupied by large groups which hindered the activity of the hydroxyl hydrogen (2,6-diacetyl-3,5-dimethylphenol; 2,6-di-*tert*-butyl-4-chlorophenol; 2,6-di-*tert*-butyl-4-cyclohexylphenol; 2,4,6-tri-*tert*-butylphenol; 2,6-di-*tert*-butyl-4-methylphenol; and 2,6-di-*tert*-butyl-4-ethylphenol). The non-reactivity of 2,6-di-*tert*-butyl substituted phenols makes possible the removal of admixed 2-*tert*-butyl substituted phenols upon treatment of the mixtures with phenyl *iso*cyanate. Thus in the preparation of 2-*tert*-butyl-4-cyclohexylphenyl-N-phenylcarbamate from a mixture of 2-*tert*-butyl-4-cyclohexylphenol and 2,6-di-*tert*-butyl-4-cyclohexylphenol, the aryl N-phenylcarbamate had a sharp m.p. and its elementary analysis indicated that only the mono-*tert*-butyl derivative reacted with the phenyl *iso*cyanate. X-ray diffraction data and m.p. are tabulated for the N-phenylcarbamates of 44 phenols. For 2-nitrophenol and the 6 non-reactive phenols (*supra*) the data refer to the original phenol. A. O. J.

Colorimetric Determination of 1-Chloro-2, 4-Dinitrobenzene as Impurity in 2, 4-Dinitroanisole. M. S. Schechter and H. L. Haller (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 326–327)—2,4-Dinitroanisole is manufactured either by methylation of 2,4-dinitrophenol or by reaction of alkali and methanol with 1-chloro-2,4-dinitrobenzene. In the second process some of the chlorodinitrobenzene may be left in the final product and, as it is a powerful skin irritant, a sensitive colorimetric method for its estimation is desired. The procedure developed is based upon the Vongerichten reaction



Place 0·5 g of each sample in photometer test-tubes marked at 25 ml. For standards of comparison use pure 2,4-dinitroanisole (free from 1-chloro-2,4-dinitrobenzene) in the following amounts:—0·5, 0·5, 0·499, 0·498, 0·497, 0·496 and 0·495 g. Weigh 50 mg of 1-chloro-2,4-dinitrobenzene into a 50-ml flask. From a burette add 5 ml of colourless pyridine to each of the samples to be analysed, and to the standard comparison tubes add in order 5, 5, 4, 3, 2, 1 and 0 ml. Immediately make the 1-chloro-2,4-dinitrobenzene up to 50 ml with pyridine, mix thoroughly and add to the standard tubes in order 0, 0, 1, 2, 3, 4 and 5 ml of this soln., which darkens rapidly and must be made fresh for each analysis and used immediately. Heat all the tubes in boiling water for 30 min. Cool, make up the liquids to 25 ml with ethanol, mix thoroughly and measure the colours in a photometer, using a No. 58 yellow filter (max. transmission at *ca.* 580mμ). The standards containing 0·5 g of 2,4-dinitroanisole and no 1-chloro-2,4-dinitrobenzene serve as blanks to balance the photometer at 100% transmission. This gives reading I and the red colour is due presumably to compound A. Place 1 ml of each of the foregoing solns. in another set of photometer tubes, dilute to 25 ml with ethanol, add 1 ml of colourless 2% alcoholic sodium hydroxide soln., mix thoroughly, stopper with corks and measure the colour as before. This gives reading II, the colour being due presumably to compound B. Plot the results of both sets of readings on semilogarithmic paper as % transmission (logarithmic ordinate) against concn. of 1-chloro-2,4-dinitrobenzene, and read the concn. of the unknown soln. from either curve. Reading II should be used when the sample is suspected of containing coloured impurities, which can be detected by visual comparison of the colour of the original sample with that of pure 2,4-dinitroanisole. Reading I may be omitted, and the samples are then heated in Pyrex tubes with pyridine, diluted to 25 ml with ethanol and 1-ml portions are placed in photometer tubes for the subsequent treatment. With experience the number of standards may be reduced, but the order of operations must be as described. The following procedure for the development of the colour of compound B serves as a qualitative test for 1-chloro-2,4-dinitrobenzene. Heat 0·5 g of the sample with 2 ml of pyridine in boiling water for 20–30 min., cool, add water in small amounts until the 2,4-dinitroanisole begins to crystallise out, dilute to *ca.* 30 ml with water, cool in ice, filter and wash the ppt. with a little cold water. Make the filtrate up to 100 ml, and to a suitable aliquot portion, according to the amount of 1-chloro-2,4-dinitrobenzene present, add 10 ml of 10% sodium hydroxide soln. and extract with 10 ml of chloroform. Wash the chloroform layer with 50 ml of 2% sodium carbonate soln. and filter through a cotton wool plug. Repeat the extraction with chloroform until the chloroform extracts no more colour, concentrate the combined chloroform extracts to *ca.* 1 ml on the water-bath and complete the evaporation at room temp. *in vacuo*. Dissolve the residue in 2 ml of 1-butanol, add 2 ml of 10% sodium hydroxide soln., shake and observe the reddish-violet colour in the 1-butanol layer. The colour is more stable if the soln. is kept cold. With a blank test for comparison, 0·01 mg of 1-chloro-2,4-dinitrobenzene can be detected in 0·5 g of 2,4-dinitroanisole. A. O. J.

Determination of Dirt in Wood Chips. Anon. (*Paper Trade J.*, 1944, **118**, *T.A.P.P.I. Sect.*, 117–119)—The T.A.P.P.I. Suggested Standard Method described is intended primarily to provide an approx. numerical evaluation for the dirt in wood chips for pulping for cellulose manufacture. Obtain by suitable means (*e.g.*, by quartering) sufficient sample to fill a 5-gallon container; stopper this, and

weigh it with the chips to the nearest 5 g. Spread out the chips on a sorting table, pick out the various types of "dirt" (*vide infra*) and place them in separate light containers. Stopper these, weigh each to the nearest 0·1 g and calculate the wts. of the respective contents as a % of the original sample, to 2 decimal places. Count as dirt every chip containing embedded foreign dirt. Calculate the "dirt rating" of the sample by multiplying the % of each type of dirt present by the following "penalty factors" for unbleached and bleached pulps, respectively:—bark, 66, 44; black knots, 6, 16; pin knots, 2, 2; red knots, 2, 2; pitch 1, 1; sawdust (not determined as dirt in the above procedure), 1, 1. The sum of the resulting values is an inverse measure of the quality of the chips.

J. G.

Inorganic

Spot Tests for Detection of Segregated Constituents in Brass and Bronze. Anon. (*Nickel Bulletin*, 1944, **17**, 83; *Metal Progress*, 1944, **45**, 296)—Three methods of U.S. origin are described. (*a*) *General Motors' Corpn.* [*Electrographic Method*]—The test sample is ground flat and placed in contact with the gelatin side of a piece of gelatin surfaced paper uniformly moistened with water containing 2% of sodium nitrate and 1% of sodium carbonate. A similar sample is placed on the back of the paper and the two are firmly pressed together in a clamp with the jaws insulated from one another. To test for iron, apply a p.d. of 10 volts between the specimens, making the test-sample the anode, for 1 minute; remove the paper and immerse it in 10% aqueous tannic acid; a purple colour shows the location of iron. To test for lead, apply similarly a p.d. of 4 volts for 15 seconds, wash the paper in 30% potassium cyanide soln. and develop it in 5% sodium sulphide soln. in 10% potassium cyanide soln.; dark brown areas indicate lead. For nickel, apply 3–4 volts for 30 seconds and develop the print in dimethylglyoxime soln. (1% soln. in 10% aqueous ammonia containing 2% of ammonium chloride). (*b*) *Revere Company*—For iron, place a drop of dilute nitric acid (1 : 1) on the spot, followed after about 1 second by a drop of dilute potassium thiocyanate soln. The usual red colour indicates iron. (*c*) *Haberfelde Company*—For lead, place a drop of 1 : 1 nitric acid on the spot, leave it until appreciable attack has occurred and then absorb it in a small piece of filter paper moistened with dilute (1 : 6) sulphuric acid. Wash out the copper-salt colour from the paper in 2% sulphuric acid and add a drop of a reagent containing 5 g of stannous chloride, 5 g of cadmium nitrate and 10 g of potassium iodide in 100 ml. A yellow or orange colour indicates lead.

S. G. C.

Colorimetric Determination of Nickel in Steel. H. L. Mauzy and H. Yellin (*Nickel Bulletin*, 1944, **17**, 85–86; *Metal Progress*, 1944, **45**, 689)—For a nickel content up to 0·8%, dissolve a 0·1 g sample in 10 ml of 1 : 1 hydrochloric acid and 10 ml of dilute nitric acid (sp.gr. 1·16). Boil, dilute to 100 ml, and to a 25 ml aliquot portion add in the following order 25 ml of water, 10 ml of 10% citric acid, 5 ml of saturated bromine water, 10 ml of 1 : 1 ammonia and 3 ml of 1% alcoholic dimethylglyoxime soln. Dilute to 100 ml. Determine the depth of colour with the aid of a photoelectric colorimeter calibrated against a range of standard steel solns. treated similarly. For higher nickel contents a smaller aliquot must be taken both of the test soln. and of the standard steel soln. used in the calibration.

S. G. C.

Colorimetric Determination of Tin with Silicomolybdate. I. Baker, M. Miller and R. S. Gibbs (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 269–271)—The method is specially adapted to the determination of small amounts of tin in steel. Weigh 10 g for % below 0·05, dissolve in 15 ml of strong sulphuric and 30 ml of hydrochloric acids diluted to 200 ml in a 250-ml Claisen flask. Add glass beads and evaporate until the H_2SO_4 just fumes and the residue is pasty. Cool, add 10 ml of strong sulphuric acid, insert a thermometer in the central neck (bulb near bottom) and a 50-ml separating funnel in the other neck; connect with a condenser delivering into a 100-ml conical flask. Introduce 10 ml of strong hydrochloric acid and 15 ml of 40% potassium bromide soln. through the funnel, then fill the latter with 40 ml of strong hydrochloric acid. Distil until the thermometer indicates 138°–143° C. Add the acid from the funnel, drop by drop, while maintaining the temperature, and finally heat to 150° C. Cool, rinse the condenser with 1 : 1 hydrochloric acid into the receiver.

Micro Method (0·02–0·2 mg of Sn)—Evaporate the distillate to less than 6 ml, dilute to 6 ml with 1 : 1 hydrochloric acid. To the boiling soln. add 2 zinc granules, boil and swirl for 1 min., add 20 ml of silicomolybdate reagent and decant within 10 sec. from the zinc into a glass-stoppered conical flask. Treat a standard soln. (0·1 mg of Sn in 6 ml) by the same procedure and compare the blue tints after 5 min.

Macro method (0·2 to 1 mg of Sn)—Evaporate the distillate to *ca.* 25 ml, dilute to 30 ml with 1 : 1 hydrochloric acid and transfer to a 250-ml conical flask. Boil with 10 zinc granules (4–5 g) as above, add 100 ml of reagent, mix and decant quickly as before, alongside a standard containing 0·5 mg of tin in 30 ml. The reagent is not reduced within 10 sec.

Intensities were measured in a photoelectric filter photometer (Fisher) and in a Duboscq comparator. The solns. conform to Beer's law up to 1 mg of tin in 30 ml; higher concns. produce weaker tints. The reagent, which should be freshly prepared each day, requires 2 stock solns. (1) Fuse 1 g of pure silica with 5 g of sodium carbonate and make up to 1 litre. (2) Make up 5·3 g of ammonium molybdate and 10 ml of strong sulphuric acid to 200 ml. (3) Dilute 10 ml of soln. (2) to 800 ml, add 2·5 ml of soln. (1), and dilute to 1 litre. Mix and set aside for ½ hr. before use. For non-ferrous metals containing more than 0·05% of tin, dissolve 1 g in 25 ml of water, 15 ml of strong sulphuric acid and 10 ml of strong nitric acid. Heat until strong fumes appear, to expel nitric acid, transfer to the Claisen flask, rinsing with 1 : 1 hydrochloric acid, and proceed as above (*cf.* ANALYST, 1943, **68**, 373).

W. R. S.

Qualitative Iron Reactions. P. Wenger and R. Duckert (*Helv. Chim. Acta*, 1944, **27**, 757–770)—The authors tabulate 105 reagents not recommended for various reasons. Recommended reactions: *Ferrous Iron*—(A) *Spot plate tests*—(1) A 2% soln. of αα′-dipyridyl in 3 *N* hydrochloric acid gives a red colour at 20° C. in neutral or ammoniacal soln. at 1 : 1·5 × 10^6. Ferric ion does not interfere. (2) A 0·025 *M* aqueous soln. of *o*-phenanthrolin gives a red colour at 20° C. in slightly acid or neutral soln. at 1 : 1·5 × 10^6. Iridium does, ferric iron

does not, interfere. (3) A 1% alcoholic soln. of dimethylglyoxime gives a red colour in ammoniacal soln. at $1 : 5 \times 10^5$. Copper, platinum, cobalt, and nickel also react; arsenic, gold, rhodium, iridium, tungsten, vanadium, and manganese interfere. (B) *Spot tests on filter paper*—(1) As (A), 1; 2 as (A), 2. (C) *Test tube reactions* (micro and macro)—(1) As (A), 1, at $1 : 10^7$. (2) As (A), 2, at $1 : 10^7$. (3) As (A), 3, at 100° C. and $1 : 5 \times 10^6$. *Ferric Iron—Microscope*—A saturated aq. soln. of pyramidon with ammonium thiocyanate and a 0·02% soln. of cobaltous chloride in 1% hydrochloric acid give a red ppt. at 60° C. in slightly acid chloride soln. at $1 : 10^4$. Rhodium, iridium, titanium, thorium, thallium, zinc, tellurous and vanadyl ion also react. (A) *Spot plate tests*—(1) A saturated aq. soln. of pyramidon gives a blue colour at 20° C. in slightly acid chloride soln. at $1 : 3 \times 10^4$. (2) Salicyl-5-sulphonic acid in 5% aq. soln. gives a violet colour at 20° C. in slightly acid soln. at $1 : 3 \times 10^5$. Titanium interferes. (3) Potassium thiocyanate (saturated soln.) gives a red colour in acid soln. at $1 : 5 \times 10^5$. A number of elements interfere. (4) Acetylacetone gives a red colour in cold acid soln. at $1 : 3 \times 10^4$. Ferrous ion gives a yellow colour; mercurous, uranyl and titanium salts interfere. (5) A 10% soln. of barium *iso*nitrosothioglycollate in *N* hydrochloric acid gives a blue colour at 20° C. in acid soln. at $1 : 10^5$. Mercurous, copper, arsenic, antimony, palladium, selenium, vanadic and thallic compounds interfere. (B) *Spot tests on filter paper*—(1) As (A) 2, at $1 : 5 \times 10^4$. (2) As (A) 3, at $1 : 10^5$. (3) As (A) 4, at $1 : 10^4$. (4) As (A) 5, at $1 : 6 \times 10^4$. (C) *Test tube reactions*—(1) As (A) 2, at $1 : 10^6$. (2) As (A) 3, at $1 : 10^5$. (3) As (A) 4, at $1 : 10^6$. (4) As (A) 5, a blue-black colour at $1 : 10^6$. W. R. S.

Determination of Iron with Nitroso-R-Salt. C. P. Sideris, H. Y. Young and H. H. Q. Chun (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 276)—To 10 ml of the soln. in a 50-ml test-tube add 0·5 ml of 10% hydroxylamine sulphate soln., a drop of 0·05% metanil yellow indicator, and 14% ammonia soln. until a pinkish-yellow colour results. Treat the soln. with 1 ml of 0·5% nitroso-R-salt soln. and 2 ml of 4 *N* sodium acetate and dilute to a known volume (*e.g.*, 20 ml). Leave for 2 to 24 hr. in a photoelectric colorimeter and measure the colour intensity with a KS-66 filter (640–700$m\mu$) and a 25-mm cell. Use a 10-mm cell with a 7·5-mm plunger for iron contents below 1μg per ml. Beer's law is valid up to 10μg of iron per ml. W. R. S.

Precision and Accuracy of Colorimetric Procedures as Analytical Control Methods. Determination of Aluminium. A. L. Olsen, E. A. Gee and V. McLendon (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 169–172)—A colorimetric procedure for the rapid determination of aluminium in leach liquors from a pilot plant has been developed. The colour produced with aurin tricarboxylic acid is assessed in a commercial photoelectric absorptiometer, using a filter transmitting light of wavelength 500 to 570$m\mu$. Factors causing variable results have been investigated and controlled, and a statistical examination of results shows that the method has a precision, measured by the average deviation of single values from the mean, of about 1%, and an overall accuracy of the order of 1 to 3%. *Reagents*: *Composite soln.*—Dissolve 154 g of ammonium acetate, 5 ml of conc. hydrochloric acid, 0·400 g of aurin tricarboxylic acid and 1 g of gum arabic in water, mix in order, and dilute to 1000 ml. Add the gum soln. cautiously to prevent foaming. The soln. deteriorates with age and in light. *Working standard soln.*—Aluminium chloride soln., 1 ml ≡ 0·01 mg of Al_2O_3. *Method*—Pipette a convenient vol. of diluted acidified sample (60 ml of conc. hydrochloric acid in 1000 ml) containing the equiv. of 0·01 to 0·06 mg of Al_2O_3 into a 25-ml blood-sugar tube, dilute to 12·5 ml and mix. Add 10 ml of composite soln., dilute to 25 ml, mix, and place the tube in boiling water for exactly 10 min. Cool in running water for 5 min. and determine the optical absorption. Prepare a calibration curve, using 1 to 6 ml portions of standard soln. The procedure as given is not satisfactory in presence of ferric iron, beryllium, chromium and phosphate. Carefully cleaned new glass tubes appear to be essential for obtaining consistent results. It is desirable frequently to include a known standard with the samples, as the instability of the composite soln. affects the accuracy of the results and makes periodic re-calibration necessary. L. A. D.

Colorimetric Determination of Osmium. E. B. Sandell (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 342–343)—The method permits the determination of traces of osmium, as in meteoric iron (3–10 p.p.m.) in 1 g of the sample. The osmium is distilled in an all-glass apparatus (*Id.*, 1934, **6**, 274). Transfer the sulphate soln. free from chloride to the round distillation flask (capacity 250–500 ml), add 5% permanganate soln. until the liquid becomes pink, then add *ca.* 0·05 g of ferrous ammonium sulphate. The volume of the soln. should now be 40 ml or less. Add a few grains of pumice, connect flask and condenser and heat slowly to boiling, making sure that higher manganese oxides dissolve. Dip the end of the condenser into 10 ml of 1 : 1 hydrochloric acid freshly saturated with sulphur dioxide. Introduce 15 ml of strong nitric acid through the funnel and collect 10 ml of distillate in 10–15 min. Transfer to a 25-ml flask, add 0·5 ml of 10% thiourea soln. and adjust the volume. After 5 min. determine the transmission of a 1-cm. layer of soln. in a photoelectric photometer, using green light. A curve must be constructed by means of an osmium tetroxide soln. in 0·1 *N* sulphuric acid (0·005% Os) by adding 0, 25 and 50μg of osmium to distillates from osmium-free nitric acid mixtures; the solns. obey Beer's law. For the determination in meteorites, 1 g is heated in a conical flask with 10 ml of 6 *N* sulphuric acid. When action is over, decant, reserve the liquid, dissolve the residue in 10 ml of hot 6 *N* hydrochloric acid, and expel this by double evaporation with 10 ml of 6 *N* sulphuric acid. Dilute the cool acid, add it to the reserved portion, and transfer to the still. The iron is oxidised with permanganate and the distillation conducted as above, the distillate being collected in 5 ml of hydrochloric-sulphurous acid; 0·3 ml of thiourea soln. is used for amounts below 10μg. The results are slightly low. W. R. S.

Determination of Germanium in Steel. A. Weissler (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 311–312)—The element is isolated by distillation and pptd. as the tannin complex (ANALYST, 1938, **63**, 388); this is considered the best method. Dissolve the steel (10 g) in 100 ml of sulphuric acid (1 : 4) and 10 ml of strong nitric acid in a 500-ml round distillation flask, the neck of which fits into a Widmer fractionating column. When solution is complete, boil gently for 30 min., then add 5 g of copper turnings and boil to destroy nitric acid and expel nitrogen oxides. Rinse down the flask to

give a vol. of 150 ml, cool in ice, add 200 ml of strong hydrochloric acid and at once connect to the distillation apparatus comprising the fractionating column, a Liebig condenser with a safety bulb attached to its lower end, and a receiver containing 100 ml of ice-cold water. Distil at the rate of a drop of constant-boiling acid per 5 sec., collecting 20–30 ml of distillate (b.p. of $GeCl_4$, 86° C.). To the distillate add 2 g of hydroxylamine hydrochloride as a reducing agent, 30 ml of fresh 5% tannin soln. during agitation, and methyl red indicator; neutralise with ammonia, barely acidify with sulphuric acid, and then add 10 drops in excess (0·08 *N* acidity). Heat nearly to boiling, set aside to cool, filter, and wash with a soln. containing 50 g of ammonium nitrate, 5 g of tannin, and 5 ml of nitric acid per litre until the chloride reaction disappears. Ignite cautiously in a tared platinum crucible and then at 600° C. for *ca.* 1 hr.; cool, evaporate with 5 drops of sulphuric acid and 3 ml of nitric acid, again heat at 600° C., and finally ignite the white residue at 900°–1000° C. for 10 min.; weigh as GeO_2. Carry out a blank assay. It was found that tannin pptn. from chloride soln. was quite satisfactory, although the original directions prescribe sulphate soln.; it is only necessary to remove all traces of chloride by washing, otherwise germanium is lost by volatilisation. Final ignition at 1000° C. (not higher) avoids high results, due perhaps to retention of sulphate. W. R. S.

Determination of Germanium. H. H. Willard and C. W. Zuehlke (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 322–324)—Two new methods were worked out. (1) *Volumetric thiogermanate method*—This is based on the reaction $K_2Ge_2S_5 + 5I_2 + 8H_2O = 5S + 2Ge(OH)_4 + 8HI + 2KI$. Treat the aqueous soln. of germanium dioxide (25 ml) with 20 ml of 8% potassium sulphide soln. previously saturated with hydrogen sulphide at 0° C. Slowly add 15 ml of 2·5 *M* acetic acid, set aside for 5 min., and pass a rapid stream of carbon dioxide to remove all hydrogen sulphide. Transfer to a large beaker, dilute to 1000 ml, add a measured excess of 0·1 *N* iodine, and after 15 min. titrate back with 0·1 *N* thiosulphate. The "scope of the method is seriously limited" by the fact that germanium is usually separated by distillation with strong hydrochloric acid, and that the alkali chloride formed by neutralisation of the distillate markedly interferes in the titration. (2) *Gravimetric 5,6-benzoquinoline method*—Benzoquinoline trioxalatogermanate is a crystalline ppt. The reagent is prepared from 10 g of the base (Eastman Kodak Co.) and 5 g of oxalic acid heated with 50 ml of water, filtered and diluted to 500 ml. Treat the hot aqueous soln. of germanium dioxide (400 ml) with 5 g of oxalic acid and 25 ml of reagent and set aside in the cold overnight. Collect the ppt., wash with a dilute soln. of oxalic acid and reagent, ignite in a platinum crucible at 700°–800° C., and weigh as GeO_2. The ppt. cannot be weighed as such because some of the reagent is co-pptd. Sodium chloride completely prevents the pptn.; probably the complex Na_2GeCl_6 is stable. The complex oxalates of tin, titanium, zirconium, and iron are also pptd. by the reagent. W. R. S.

(*Abstractor's Note*—These two methods appear to present no practical advantages over the simpler tannin method. See preceding abstract.)

Potentiometric Determination of Magnesium in Magnesite and Dolomite. A. J. Boyle, C. C. Casto and R. M. Haney (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 313–314)—The method is very quick, requires no filtration, and is claimed to be as accurate as the gravimetric determination. Heat 2 g of the sample with 20 ml of perchloric acid (1 : 1) in a 400-ml beaker and evaporate to dryness. Boil with 100 ml of water and 10 drops of hydrochloric acid, add calcium carbonate (A.R.) and boil to expel carbon dioxide. Cool, add 100 ml of alcohol and 2 ml of thymolphthalein indicator and transfer to the titrating vessel (glass electrode and mechanical stirrer). Titrate the boiling-hot soln. with carbonate-free *N* sodium hydroxide soln. The indicator shows the approach to the end-point, which is finally attained by addition of 0·1-ml portions of alkali. The greatest deflection of the galvanometer for 0·1 ml is taken as the end-point, or a graph may be constructed. W. R. S.

Physical Methods, Apparatus, etc.

The Polarographic Determination of Small Amounts of Nitrobenzene in Aniline. J. Haslam and L. H. Cross (*J. Soc. Chem. Ind.*, 1944, **63**, 94–95)—The normal method for the determination of nitrobenzene in aniline involves the measurement of the amount of standard titanous soln. reacting with the nitrobenzene in the sample. This involves two titrations of titanous soln. with standard ferric soln. In chemical plant control work this test has not proved satisfactory, particularly for the precise determination in aniline of amounts of nitrobenzene of the order of 0·025%. Novak's polarographic method (*Coll. Czech. Chem. Comm.*, 1939, **11**, 573) is claimed to determine 0·00015% to 1% of nitrobenzene in aniline, the reduction potential of nitrobenzene being about 0·46 volt. This method, however, gives troublesome maxima above 0·05% of nitrobenzene. The following method has been found to give very satisfactory results for the range 0·01% to 0·05% of nitrobenzene. To 2 ml of the sample add 0·5 ml of a soln. which contains 0·1 g of nigrosine in 100 ml. of conc. hydrochloric acid. Transfer the liquid to the cell of a polarograph (Cambridge) and obtain the polarogram over the range 0 to 1·4 applied voltage. Calibrate, using specially purified aniline to which known amounts of nitrobenzene have been added. The purified aniline may be prepared by double distillation and checked polarographically for absence of nitrobenzene. B. S. C.

Spectrographic Determination of Small Amounts of Impurities in Magnesium Chloride. M. F. Wilson (*J. Opt. Soc. Amer.*, 1944, **34**, 229–233)—A close control of the minor impurities in magnesium chloride is necessary for the successful deposition of metallic magnesium. Boron, silicon, iron, manganese, aluminium, copper, sodium and calcium may be rapidly and accurately determined spectrographically. An important feature of the method is the use of molybdenum as an internal standard. Routine samples are usually in the form of a water soln. of sp.gr. approx. 1·325. To each volume of sample soln. taken for test an equal vol. of an aq. soln. of ammonium molybdate is added, the latter containing the equivalent of 2 mg of molybdenum per ml. After dilution of the mixed soln. to give an approx. concn. of 50 g of magnesium chloride per litre, 0·05 ml of the soln. is absorbed on each of a pair of ¼ in. diam. pure graphite rods, which are then oven dried (80–90° C.) for 1 hr. The spectrum is excited using a 2300 volt, 2·25 amp. A.C. arc and photographed with a large quartz spectrograph. Plates are calibrated (density/intensity) using a 220 volt, 2·5 amp. D.C. iron arc. The single iron line 3083·75A is sufficient to calibrate

over the whole wavelength range of interest (3100 to 2500A), since the gamma value of the Eastman antihalation process plates used is constant over this range. Using this calibration curve, analytical curves for the various impurities listed above may be prepared from the spectra of synthetic standard solns. containing known concns. of the various impurities. Redistilled metallic magnesium, 99·99% pure, was dissolved in hydrochloric acid to form a spectrographically pure magnesium chloride soln. for the prepn. of these standards. Suitable line pairs for the analyses are as follows.

Impurity	Line pair: Impurity line	Line pair: Molybdenum line	Concn. Range g/litre impurity
NaCl	Na 3302·4A	3208·9A	0·5 to 30·0
$CaCl_2$	Ca 3181·3	3208·9	0·5 to 30·0
,,	Ca 3158·9	3208·9	0·25 to 10·0
Cu	3247·5	3208·9	0·0008 to 0·2
,,	3273·9	3208·9	0·002 to 0·5
Al	3082·2	3116·1	0·02 to 2·0
B	2497·7	2538·5	0·0002 to 0·4
Si	2506·9	2538·5	0·001 to 0·2
,,	2516·2	2538·5	0·005 to 0·5
Fe	2599·4	2538·5	0·0008 to 0·2
,,	2563·5	2538·5	0·02 to 5·0
Mn	2605·7	2538·5	0·0002 to 0·03

An accuracy of 10% of the amount present has been maintained with daily analyses over a period of a year. Complete analysis of a sample in triplicate takes 2½ hr. B. S. C.

Spectrographic Analysis. Photographic Aspects. III. Graphical Calculators applied to Plate Calibration using Relative Intensities. N. S. Brommelle and H. R. Clayton (*J. Soc. Chem. Ind.*, 1944, **63**, 83–89)—As an alternative to the use of analysed standard alloys on each plate, calibration may be effected by the relative intensity method used in conjunction with a calculator (Amstein, *J. Soc. Chem. Ind.*, 1943, **62**, 51). This results in a considerable saving in time, over 90 min. per plate in the examples described. The principle, construction and method of using three types of calculator are described in detail, and the relative merits of the calculators are discussed. The results obtained by these methods are as satisfactory as with the analysed standard method. B. S. C.

Systematic Polarographic Metal Analysis. J. J. Lingane (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 147–152)—In a systematic scheme for the polarographic determination of *ca.* 12 metallic elements, a few preliminary group separations are a practical necessity, otherwise interferences become too numerous to be avoided readily. Fortunately the sulphide separations of the classical qualitative analytical scheme provide groups of metals which are as convenient as any for subsequent polarographic analysis. All members of the copper group (copper, bismuth, lead and cadmium) may be determined simultaneously from a single polarogram, using an acid tartrate supporting electrolyte, provided that they are present at very nearly equal concns. This is rarely to be expected, and a modified procedure must usually be adopted. First, if the concns. increase in the order copper, bismuth, lead, cadmium, a complete analysis of the group can be achieved by recording four polarograms of the same soln. with successively smaller galvanometer sensitivities; this magnifies in turn the wave of each constituent to a value that will allow accurate measurement. When the concns. increase in the opposite order, however, the larger waves of the nobler metals, such as copper, interfere with or mask completely the smaller waves of the baser metals, such as lead; in such instances it is necessary to eliminate the waves of the nobler metals. Electrodeposition at controlled cathode potential constitutes an excellent means of doing this. Furthermore the use of a mercury cathode is the most convenient, since this enables the necessary cathode potential to be calculated from a preliminary polarogram on a soln. of the unseparated group. The apparatus and technique for these separations are described in detail and the method is illustrated with typical examples. B. S. C.

Reviews

PHYSICO-CHEMICAL METHODS. By Prof. J. REILLY, M.A., D.Sc., F.Inst.P., F.R.C.Sc.I., F.R.I.C., and Prof. W. N. RAE, V.D., M.A., Sc.D., F.R.I.C. Fourth Edition. Vol. I. Pp. ix + 610; Vol. II. Pp. vii + 585. London: Methuen. 1943. Price £4 4s.

These two volumes represent a considerable effort to bring together the numerous physico-chemical methods now available. Sometimes the authors have been content with descriptions of made-up apparatus on the market and their mode of operation instead of giving more fundamental details of their construction. There is a tendency now-a-days to use these ready-made sets and to put implicit trust in the results they give, which, owing to a lack of knowledge of the construction of the instruments and their shortcomings, may be far from accurate.

The subject-matter is rather uneven in both the treatment and the space accorded to the different topics. In some instances the treatment is thorough and generally excellent, whereas in others it is sketchy, inadequate, occasionally inaccurate and sometimes out-of-date. This perhaps is inevitable in a comprehensive work of this type, seeing that in these days physical chemists are tending to become specialists in their own particular branches of the subject and are often almost ignorant of others.

Thus, whereas balances, distillation apparatus and the various types of pumps are extremely well discussed, electrochemical technique, including the various electrometric methods of analysis, receive in general only inadequate treatment. Instead of describing the Kerridge glass electrode in some detail and the measuring apparatus produced by a well-known firm of instruments-makers the authors would have done better to describe the simple

bulb electrode and the details for the construction of a simple, relatively inexpensive, thermionic valve circuit suitable for use in the determination of *p*H. It is true that the antimony electrode may be used to determine *p*H values within 0·05 *p*H, as stated, if carefully calibrated, but there is no mention of the fact that it may lead to appreciable errors if certain disturbing factors are associated with the solution under test.

In a few instances the treatment is extensive, so much so that applications to the experimental plant scale and occasionally to the industrial scale find a place. The multiplicity of the subjects dealt with will certainly continue to render the work of inestimable value in chemical, and particularly in research laboratories. As a rule sufficient theoretical matter is included not only to make the methods themselves intelligible but to indicate the intrinsic value of data obtained from the use of such methods. Useful lists of references are given to the standard works on the particular branches of the subject, but some of them are far from complete, as many authoritative monographs have been omitted.

Some omissions of important physico-chemical methods have been noted, although it may be that the authors consider that they lie more within the domain of pure physics, *e.g.*, the mass spectrograph and much of the technique involved in radioactive changes and in the study of rare gases, magneto-chemistry and photo-chemistry. One feels, however, that phase rule investigations involving alloy formation and crystallisation from solutions might have found a more prominent place. But, as already stated, omissions and shortcomings are bound to occur in so compendious a treatise as this. The work would be a useful addition to any experimental chemist's library and its increased appeal since the publication of its first edition in 1926 is excellent proof of the real value that chemists attach to it. The authors are to be warmly congratulated on its continued success. H. T. S. BRITTON

PLANTS AND VITAMINS. By W. H. SCHOPFER. Authorised translation by NORBERT L. NOECKER. Pp. xiv + 293. Waltham, Mass., U.S.A.: The Chronica Botanica Co.; London: Wm. Dawson & Sons, Ltd. 1943. Price $4.75.

The necessity of vitamins in the diet of animals to ensure normal growth and the maintenance of a healthy condition is now an established fact based on many years of biochemical research, which showed that plants synthesised vitamins and the animals utilised them. Only in recent years, however, was it realised that vitamins also played an important part in plant physiology and were not merely useless substances from the point of view of the plant growth and of benefit only to animals. This volume constitutes a comprehensive survey of the existing knowledge on the subject of the functions of vitamins in plant growth. The subject matter is presented in an attractive style with abundant references to the relevant literature at the end of each chapter.

The author, a professor of botany, states in his introduction "that it is his aim to point out the importance of vitamins in plants to botanists, particularly to plant physiologists and animal physiologists." It might therefore be expected that the book would be entirely botanical in its treatment, but this is not so, and the book contains much information of interest to the biochemist.

The book is divided into three parts. Part I is devoted to a study of the biosynthesis and distribution of vitamins in the higher plants. It also contains a description of the methods of attack which have been employed in investigations into this subject. The need of vitamins in embryo, leaf, and in root cultures is also discussed, and full experimental details of the technique employed are given. In this part the author discusses at some length the different methods of classification that have been suggested for the different growth substances such as vitamins, auxins, etc. This chapter serves to emphasise the extreme difficulties of this problem of classification, particularly in view of the ever-increasing number of different types of growth factors which are being discovered.

Part II is devoted to investigational work on the function of vitamins in the growth of micro-organisms. A number of micro-organisms are unable to synthesise the vitamins that are necessary for their growth, and therefore when these organisms are grown on a synthetic medium it is necessary that the appropriate vitamins be included in the nutrients employed in the preparation of the medium. This work is of great value to micro-biologists and to biochemists engaged in vitamin assays employing micro-organisms.

In Part III general problems involving vitamins in connection with plant growth are discussed. It includes the rôle of vitamins in agriculture and horticulture, but many agricultural chemists will regret that more information is not available on the subject of the

function of vitamins in the higher plants, particularly from the point of view of the use of vitamins in fertilisers.

This section includes a chapter on micro-organisms as "test objects" for vitamins. In view of the increasing use of micro-biological methods for vitamin assays, this is an important chapter and one which in a subsequent edition might be enlarged very considerably; it could be made very much more valuable if full experimental details of the procedures involved could be given. As many of the methods are still in the experimental stage, these details can scarcely be expected to appear in this edition. J. HUBERT HAMENCE

SUPPLEMENT TO THE EXTRA PHARMACOPOEIA. Vol. I, 22nd Ed., 1941. Pp. 48. London: The Pharmaceutical Press. 1943. Price 2s.

The large number of changes in the contents of the British Pharmacopoeia and the British Pharmaceutical Codex since May, 1941, and also the publication of the twelfth edition of the United States Pharmacopoeia and the seventh edition of the United States National Formulary, have made it necessary to amend much of the matter contained in Volume I of the twenty-second edition of the Extra Pharmacopoeia. This booklet summarises in convenient tables the main alterations.

The fifteen sections are devoted to a Summary of the Principal Changes made by the 4th, 5th and 6th Addenda to the B.P. 1932; Additions in the 2nd, 3rd, 4th and 5th Supplements to the B.P.C. 1934; Deletions from the B.P.C. 1934; Amendments in the 2nd, 3rd, 4th and 5th Supplements to monographs of the B.P.C. 1934; Preparations of the National War Formulary, 1943; Articles added to the U.S.P. XII; Articles deleted from the U.S.P. XII; Articles in the U.S.P. XII having new Titles; Articles added to the N.F. VII; Articles deleted from the N.F. VII; Articles in the N.F. VII having new Titles. There is also a résumé of recent Statutory Orders affecting supplies of drugs, some new Proprietary Names, and a list of additional approved names for substances that have hitherto been known by other names, and the supplement ends with the recently published corrigenda to Vol. I, which contains a few corrections of importance.

The booklet is well produced and of a convenient size, and all who require up-to-date information of official preparations should obtain this necessary adjunct to the invaluable "Martindale." JOHN ALLEN

INAUGURAL MEETING OF THE MICROCHEMICAL GROUP

IN view of the present uncertain conditions and of the extreme difficulties of travelling long distances, the Council has decided to postpone the inaugural meeting of the Microchemical Group until the day of the Ordinary Meeting of the Society in October. Members of the Group will receive notification of the meeting in due course.

PROPOSED FORMATION OF A GROUP DEALING WITH PHYSICAL METHODS OF ANALYSIS

IN pursuance of the policy for the formation of Groups for special branches of analytical chemistry proposed by the Council and approved by a meeting of the Society on November 3rd, 1943, the Council has had under consideration a proposal to form a Group dealing with physical methods of analysis. The Group would deal with such methods as for example:

1. Spectrographic methods
   (*a*) Emission spectrograph; (*b*) U.V. and visible absorption spectrograph; (*c*) Infra red absorption spectrograph; (*d*) Mass spectrograph.
2. Quantitative photometric methods by means other than spectrophotometry.
3. Polarographic methods.
4. X-Ray diffraction.

The Council's decision as to the formation of the Group will depend on the number of members of the Society desirous of joining it. Members of the Society who wish to become members of the Group are asked to notify the Hon. Secretary of the Society, 7/8, Idol Lane, London, E.C.3.

DETERMINATION OF FLUORINE IN FOODS

THE Report (pp. 243–246 in the August ANALYST) is now available as a reprint. Obtainable from the Editor. Price: Members 1/6; Non-Members 2/-; Prepaid.

ADVICE TO AUTHORS

THE Council has approved the following notice by the Publication Committee, which is here given in condensed form.

The Society publishes papers concerned with all aspects of analytical chemistry, inorganic and organic, as, for example, food and drugs analysis, analysis of water (including its bacteriological examination), gas analysis, metallurgical assays, biological standardisation and micro-analysis. Papers on these and allied subjects may be submitted for presentation and publication; they may:

(1) Record the results of original investigations into known methods or improvements therein;
(2) Record proposals for new methods and the investigations on which the proposals are based;
(3) Record analytical results obtained by known methods where these results, by virtue of special circumstances, such as their range or the novelty of the materials examined, make a useful addition to analytical information;
(4) Record the application of new apparatus and new devices in analytical technique and the interpretation of results.

Communications.—Papers (which should be sent to the Editor) will normally be submitted to at least one referee, on whose advice the Publication Committee will be guided as to the acceptance or rejection of any communication. Papers or Notes accepted by the Publication Committee may not be published elsewhere except by permission of the Committee.

Abstracts.—The MS. should be accompanied by a brief abstract of about 100 to 150 words indicating the scope and results of the investigation.

Notes on the writing of papers for THE ANALYST

Manuscript.—Papers and Notes should preferably be typewritten.

The title should be descriptive and should set out clearly the scope of the paper.

Conciseness of expression should be aimed at; clarity is facilitated by the adoption of a logical order of presentation, with the insertion of suitable paragraph or sectional headings.

Generally, the best order of presentation is as indicated below:

(*a*) General, including historical, introduction.
(*b*) Statement of object of investigation.
(*c*) Description of methods used. Working details of methods are usually most concisely and clearly given in the imperative mood, and should be given in this form, at least while economy of paper is pressing, *e.g.*, "Dissolve 1 g in 10 ml of water and add . . .". Well-known procedures must not be described in detail.
(*d*) Presentation of results.
(*e*) Discussion of results.
(*f*) Conclusions.

To be followed by a short summary (100 to 250 words) of the whole paper: items (*e*) and (*f*) can often be combined.

Illustrations, diagrams, etc.—The cost of setting up tabular matter is high and columns should therefore be as few as possible. Column headings should be brief or replaced by a number or letter to be used in combination with an explanatory footnote to the table.

Sketches or diagrams should be on white Bristol board, not larger than foolscap size, in Indian ink. Lettering should be in light pencil.

Tables or graphs may be used, but normally not both for the same set of results. Graphs should have the co-ordinate lines clearly drawn in ink.

References.—References should be numbered serially in the text and collected in that order under "REFERENCES" at the end of the paper. They should be given in the following form:

1. Dunn, J. T., and Bloxam, H. C. L., *J. Soc. Chem. Ind.*, 1933, **52**, 189T.
2. Allen, A. H., *"Commercial Organic Analysis,"* Churchill, London, 1882.

Notes on the Presentation of Papers before Meetings of the Society are appended to the "ADVICE," copies of which may be obtained on application to the Secretary, 7/8, Idol Lane, London, E.C.3.

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PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

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...e Society of Public Analysts and other Analytical Chemists by W. Heffer & Sons Ltd., ..., Cambridge. **Communications to be addressed to the Editor, C. Ainsworth ... The Close, Weedon, Aylesbury, Bucks.**