SEPTEMBER, 1928 Vol. LIII., No. 630.

THE ANALYST

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

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

XII. Observations on the Pyrosulphate-Hydrolysis Method.

By W. R. SCHOELLER and E. F. WATERHOUSE.

(*Read at the Meeting, May* 2, 1928.)

The pyrosulphate-hydrolysis method, an investigation of which was projected in Sect. I (*J. Chem. Soc.*, 1921, **120**, 1929), is the procedure consisting in the "decomposition of the mineral by fusion with alkali pyrosulphate followed by prolonged boiling of the solution of the melt in order to precipitate the earth acids." This process is still in general vogue amongst mineralogists and technical chemists.

The results of the investigation are recorded in this Section. As regards the scope of the work, we reached the conclusion that the accuracy attainable in the earth acid and zirconia separation should be the primary object of our inquiry. Hydrolysis has been generally recognised as the means for effecting this separation (see Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, Stuttgart, 1912, p. 271). Hence, at an early stage of this series of researches, Schoeller and Powell (Sect. II., *J. Chem. Soc.*, 1921, **120**, 1931) thought themselves justified in saying that the method is "so far the only one available for separating zirconium from tantalum and columbium." This statement would imply that the method is sound, but, as a matter of fact, we have found no published data establishing its reliability. Subsequent experience has taught us that it should be re-investigated, in common with other methods of earth-acid analysis that have long led a sheltered existence in the text-books.

The quantitative investigation of the behaviour of titania and earth acid mixtures in the pyrosulphate-hydrolysis process formed the next important part of our research. Observations on certain other separations, and on the method in general, conclude this Section.

A. ZIRCONIA AND EARTH ACIDS.—For purposes of orientation, we conducted four separations of tantalic, and four of niobic, oxide from zirconia. The acidity of the liquid was the only variable, other conditions being kept constant. The mixed oxides (0·5 grm.) were fused with 5 grms. of potassium bisulphate, and the cold product disintegrated with water. The volume was adjusted to 500 c.c. with dilute sulphuric acid of the required strength and the liquid boiled under reflux for 2 hours. The solution was then filtered, and an aliquot part of the filtrate titrated with 0·5 *N* ammonia against methyl orange. The acidity thus found is herein given in grms. of H_2SO_4 per 100 c.c.

The hydrolysis precipitate, *HP*, after being washed and ignited, was extracted with acidulated water, then ignited and weighed. It was then tested for zirconia by Schoeller and Powell's method (Sect. II, *loc. cit.*); in the case of the tantalum precipitates, three successive potassium carbonate fusions were made, and the residue Z^3 from the last fusion weighed as ZrO_2; the niobium precipitates were fused twice, and Z^2 weighed:

	Taken.					
Exp.	Ta_2O_5.	ZrO_2.	Acidity.	HP.	Z^3.	(HP–Z^3.)
1	0·2519	0·2509	1·47	0·3249	0·0815	0·2434
2	0·2526	0·2542	2·09	0·3222	0·0754	0·2468
3	0·2522	0·2531	3·43	0·3127	0·0475	0·2652
4	0·2539	0·2508	4·50	0·2970	0·0325	0·2645
	Nb_2O_5.				Z^2.	(HP–Z^2.)
5	0·2501	0·2521	0·99	0·3304	0·0803	0·2501
6	0·2500	0·2532	2·0	0·3206	0·0624	0·2582
7	0·2506	0·2516	2·88	0·3017	0·0509	0·2508
8	0·2500	0·2528	3·53	0·2830	0·0390	0·2440

The last column has been inserted as a check, as (HP–Z) should agree with the M_2O_5 taken (unless, like titania, zirconia interferes with the hydrolytic precipitation of the earth acids, which obviously is not the case). The differences are due to known sources of error, such as possible incomplete hydrolysis, retention of a little tantalum by Z^3, and introduction of impurities (Pt, SiO_2) into the precipitates. The determination of these relatively small errors would have served no useful purpose, in view of the serious co-precipitation of the zirconia as disclosed by the tests. In the subsequent experiments, *Z* was tested (by a new method yet to be published) for small quantities of residual pentoxide, and a deduction made where necessary.

The curve obtained by plotting the amount of co-precipitated zirconia against the acidity is practically a straight line which, on extrapolation, intersects the acidity axis at 6·5. This acidity was therefore aimed at in Exps. 9 and 10, which were otherwise conducted along precisely the same lines as the preceding:

	Taken.					
Exp.	M_2O_5.	ZrO_2.	Acidity.	HP.	Z.	(HP–Z.)
Ta9	0·2520	0·2512	7·12	0·2632	0·0126	0·2506
Nb10	0·2516	0·2524	6·46	0·2500	0·0095	0·2405

These tests indicate merely a decrease in the quantity of co-precipitated zirconia at a stage where the precipitation of the earth (especially niobic) acid is hardly complete.

We were induced next to try the effect of re-treating the hydrolysis precipitate, by certain statements in the literature to the effect that a zirconium- (and iron-) free precipitate results (*cf.* Sect. I, *loc. cit.*, where "acidified" should be inserted in line 23, p. 1929, thus: "the *acidified* filtrate is boiled under reflux, any zirconium remaining in solution"). In Exps. 11 and 12, the hydrolysis precipitate, HP^1, obtained was submitted to exactly the same treatment as the original oxide mixture, yielding a purified precipitate, HP^2, which was tested for zirconia (Z):

	Taken.					
Exp.	M_2O_5.	ZrO_2.	Acidity.	HP.	Z.	(HP^2–Z.)
Ta 11	0·2541	0·2531	3·72	HP^1 0·2926	—	—
,,	—	—	3·60	HP^2 0·2626	0·0155	0·2471
Nb 12	0·2525	0·2518	3·67	HP^1 0·2800	—	—
,,	—	—	3·75	HP^2 0·2531	0·0112	0·2419

The tests prove re-treatment of HP^1 to be less effective than the preceding hydrolyses at a higher acidity.

Simple hydrolysis having failed to achieve a separation, we turned to Weiss and Landecker's sulphurous acid method (*Z. anorg. Chem.*, 1909, **64**, 72). This consists in treating the "strongly acid" (no strength specified) liquor, containing the disintegrated pyrosulphate melt, with sulphurous acid until the precipitate flocculates, and heating only to incipient boiling. By working in this manner, they claim to be able to precipitate the earth acids quantitatively and free from other elements (except titanium). In our check tests the solutions were adjusted to 400 c.c., treated with sulphurous acid (which did not induce a decided flocculation), heated to the boiling point, left to settle, and filtered:

	Taken.				
Exp.	M_2O_5.	ZrO_2.	HP.	Z^3.	(HP–Z^3.)
Ta 13	0·2503	0·2509	0·2183	—	—
Nb 14	0·2517	0·2546	0·2110	—	—
Ta 15	0·2527	0·2539	0·2876	—	—
Nb 16	0·2536	0·2510	0·2500	—	—
Ta 17	0·2528	0·2507	0·2800	0·0528	0·2272
Nb 18	0·2520	0·2520	0·2553	0·0225	0·2328

The procedure proved troublesome, filtration being almost impracticable without the addition of considerable filter pulp (especially in Exps. 13 and 15); the filtrates were cloudy, and the recoveries so erratic that the zirconia determinations in the precipitates seemed purposeless. In Exps. 15 to 18 the fusion product was re-fused with 5 c.c. of strong sulphuric acid. The co-precipitation of zirconia in tests 17 and 18 was more pronounced than in tests 9 to 12. We must conclude that Weiss and Landecker's process, as a separation of the earth acids from zirconia, is a failure.

In the final set of tests the pyrosulphate melt, after having been re-fused with 3 to 5 c.c. of strong sulphuric acid, was extracted with cold water. The procedure was adopted on account of a few statements in the literature, of which the following is an example: "Tantalic and columbic acids are quite completely separated from the bases with which they may be combined, by fusion with potassic bisulfate, and subsequent treatment with cold water. The addition of 5·0 per cent. of sulfuric acid does not change this deportment" (Headden, *Proc. Colo. Sci. Soc.*, 1917, **11**, 185). Working in this manner we obtained low earth-acid results; in other words, they are not precipitated completely unless the solution is boiled for some time:

	Taken.		
Exp.	M_2O_5.	ZrO_2.	*P*.
Ta 19	0·2500	0·2523	0·2392
Nb 20	0·2523	0·2534	0·2384
Ta 21	0·2509	0·2517	0·2335
Nb 22	0·2517	0·2507	0·1832

This concludes the account of our work on the zirconia and earth acid separation, the outcome of which is, that no accurate separation was achieved by any of the modifications tried. We shall return to the subject in the general criticism of the pyrosulphate-hydrolysis process (*vide infra*). One final observation may here be made, namely, that in every case the tantalic acid adsorbed more zirconia than did the niobic acid at the same acid concentration. This appears to be a rule of general applicability.

B. TITANIA AND EARTH ACIDS.—The first part of Sect. IX (ANALYST, 1927, **52**, 625) deals with the more recent attempts at solving the problem of this separation; we can now complete that review in a few lines by an account of the earlier efforts. Apart from Marignac's endeavours towards an approximate separation of titanium from niobium (*Archives des Sci. phys. et nat.*, 1867, **29**, 265), these were mainly directed to the application of the pyrosulphate-hydrolysis method, Rose prescribing extraction of the fused product with cold water, whilst Hermann favoured extraction at higher temperature. The treatment was held to separate titania from the earth acids. The fallacy of this belief was gradually recognised, though meanwhile the faulty procedure had become responsible for a number of incorrect analyses. A few mineralogists were fortunately able to rectify their original statements; thus, Prior (*Min. Mag.*, 1908, **15**, 80–84) and Headden (*Proc. Colo. Sci. Soc.*, 1917, **11**, 177–183) reported independently that they had been led astray in their analysis of the same mineral (strüverite, approximately $FeO.(Ta,Nb)_2O_5.4TiO_2$), in that they failed to detect the earth acids and inferred the presence of zirconia. The facts are, that titania is rendered soluble by bisulphate fusion and subsequent treatment with cold water or dilute acid, whilst the earth acids, similarly treated, remain substantially insoluble. These properties no longer persist when the oxides are in admixture: there is most pronounced "loss of individuality." If the earth acids predominate, a large proportion of the titania remains in the insoluble residue, but the solution contains earth acid as well as titania. Mixtures, of which titania forms more than one-half, may dissolve in the cold to a perfectly clear solution. But, whatever the relative proportions of the three oxides, they are precipitated together quantitatively by sufficiently protracted boiling, at a fairly low degree of acidity of the solution.

The above observations being of a qualitative nature, we undertook a quantitative investigation of the hydrolytic precipitation, in the hope of gleaning some facts of analytical interest. In the tests tabulated below, the hydrolysis precipitates *HP* were obtained, and the acidity determined, in exactly the same manner as in Exps. 1 to 8. The distribution of the titania was ascertained colorimetrically, either in the hydrolysis precipitate or in the filtrate therefrom, *i.e.* in the fraction carrying the smaller amount of the titania; the pentoxide content of *HP* was taken by difference:

	Taken.					
Exp.	Ta_2O_5.	TiO_2.	Acidity.	*HP*.	TiO_2 in *HP*.	Ta_2O_5 in *HP*.
23	0·2528	0·2538	0·79	0·5032	0·2509	0·2523
24	0·2512	0·2529	2·03	0·4694	0·2264	0·2430
25	0·2517	0·2542	2·74	0·3712	0·1850	0·1862
26	0·2540	0·2528	3·98	0·2743	0·1356	0·1387
	Nb_2O_5.					Nb_2O_5 in *HP*.
27	0·2530	0·2522	1·11	0·4959	0·2494	0·2465
28	0·2506	0·2522	2·11	0·4644	0·2188	0·2456
29	0·2504	0·2519	2·88	0·4336	0·1908	0·2428
30	0·2518	0·2546	3·86	0·3930	0·1569	0·2361

The tabulation proves that no separation took place, and that precipitation was practically total after two hours' hydrolysis at the lowest acidity. When the precipitated quantities are plotted against the acidity, the tantalum and the two titanium precipitation curves are found to be approximately coincident: tantalum and titanium seem even to have lost their separate identity in Exps. 23 to 26. The drop in the niobium curve, on the other hand, was so gradual that we thought hydrolysis at a higher acidity might possibly achieve a preliminary separation into two fractions, containing the one oxide as the main constituent, and the other as the subordinate. Two tests were made with each pentoxide :

Exp.	M_2O_5.	TiO_2.	Acidity.	*HP*.	TiO_2 in *HP*.	M_2O_5 in *HP*.
Ta 31	0·2554	0·2505	8·05	0·1829	0·0457	0·1372
Ta 32	0·2500	0·2536	14·85	0·1110	0·0178	0·0932
Nb 33	0·2509	0·2520	10·50	0·1713	0·0325	0·1388
Nb 34	0·2509	0·2548	15·60	0·1135	0·0199	0·0936

The results are quite discouraging, as they shew that, though the earth acids were very incompletely precipitated, they carried down, even then, sufficient titania to deprive the process of any practical value.

It will be noticed that the Ta_2O_5 content of *HP* is practically the same in Exps. 26 and 31, which means a decided break in the tantalum curve. Now it should be mentioned that Exps. 31 to 34 were done at a later period than Exps. 23 to 30; 23 to 26 were carried out simultaneously, as also 27 to 30. Upon this fact we base an explanation for the irregular curve. We submit that balanced reactions, such as these hydrolyses, do not yield the same or proportional results to different operators following the same procedure, or even to the same operator at different times, the equilibrium being determined by a combination of minor factors that evades human control: "*différences insaisissables*," "*réaction assez capricieuse*," to quote Marignac (*loc. cit.*) on similar reactions. We have had a previous occasion to express this opinion (Sect. III, ANALYST, 1924, **49**, 216), when commenting on the erratic reduction of niobic oxide by zinc.

C. ZIRCONIA AND TITANIA.—The interference of zirconium with the hydrolytic precipitation of titanium has been known for some time past, but not studied to any great extent. We conducted 4 tests (35 to 38) under the same conditions as Exps. 1 to 8; 0·25 grm. ZrO_2 and 0·25 grm. TiO_2 were taken for each test, and the acidity adjusted to 1, 2, 3, and 4 grms. of H_2SO_4 per 100 c.c., respectively. The solutions, which were quite clear while cold, remained so after one hour's boiling, when the tests were interrupted. The solution in test 35, after cooling, was cautiously neutralised to slight cloudiness; this was just cleared with dilute sulphuric acid, and the solution again boiled for an hour. In Exp. 39, 0·25 grm. of titania was hydrolysed for one hour in 500 c.c. of approximately 1 per cent. sulphuric acid, precipitation setting in before the liquid began to boil:

	Taken.			
Exp.	TiO_2.	ZrO_2.	Acidity.	*HP.*
35	0·2507	0·2533	0·38	slight, colloidal
39	0·2522	none	0·94	0·2490

The small precipitate in Exp. 35 filtered so poorly that it could not have been adequately washed; we confined ourselves to the acidity determination in a portion of the filtrate. A comparison of the conditions and results of the two tests proves the powerful interference of zirconia with the hydrolysis of an equal weight of titania, even in a feebly acid sulphate solution.

Hillebrand (*Bull. Geol. Survey, U.S.A.*, No. 422, 136) observes that the effect of association is most marked, even in acid acetate solution (Gooch's method for titania), in that "0·2 per cent. of ZrO_2 was able to prevent precipitation of 0·3 per cent. of TiO_2." In view of this complex-formation, a separation process based on hydrolysis, such as that proposed by Streit and Franz (*J. prakt. Chem.*, 1869, **108**, 65), must be unsound in principle. They hydrolyse a sulphate solution diluted with an equal volume of acetic acid, but do not state whether the free mineral acid should be neutralised; only one check analysis is quoted, and this gave an indifferent result.

D. EARTH ACIDS, ZIRCONIA, AND TITANIA.—Having proved the strong interference of zirconium in the precipitation of titanium, we inferred that zirconium would probably accentuate the disturbing effect of titanium in the hydrolysis of the earth acids. In order to verify this assumption we conducted two tests in the same manner as before, with ternary mixtures, one containing tantalic oxide, and the other, niobic oxide:

	Taken.				
Exp.	M_2O_5.	ZrO_2.	TiO_2.	Acidity.	*HP*.
Ta 40	0·1011	0·2515	0·1515	1 to 2	none after 2½ hours
Nb 41	0·1007	0·2518	0·1511	1·74	0·0569

In spite of the low acidity, the precipitation of the titania *plus* earth acid was entirely checked in test 40, and most incomplete in 41, the *HP* containing 0·015 grm. of niobium pentoxide and the balance being chiefly titania. We purposely made up mixtures rich in zirconia, so as to obtain a decided indication of its influence. Our findings were confirmed by the late Dr. Hillebrand, who, in a private communication, wrote as follows: "Another evidence of the unreliability of the dilute sulphuric-sulphurous acid hydrolysis was noticed by us in some recent tests in which zirconium entirely prevented the separation of titanium in one test, and of titanium and the earth acids in another."

The evidence here given enables us to contradict Meyer and Hauser's statement (*op. cit.*, p. 271), that the pyrosulphate-hydrolysis method affords a "good separation" of titanium, niobium, and tantalum from zirconium.

E. IRON AND EARTH ACIDS.—The strong adsorption of iron by the earth-acid precipitate that invariably takes place in the pyrosulphate-hydrolysis process is familiar to every analyst who has applied it to the analysis of tantalite; the white hydrolysis precipitate, on digestion with ammonium sulphide (a treatment supposed to eliminate tin and tungsten; *cf.* Sect. VIII, ANALYST, 1927, **52**, 506), always turns bluish-green to dark green, the ferric compound contained in it being converted into ferrous sulphide. Further proof that the separation in question is incomplete is not required. Now Weiss and Landecker (*loc. cit.*, under A) claim that their sulphurous-acid method yields an iron-free precipitate, no doubt because reduction to non-hydrolysed ferrous salt takes place. We investigated this claim by the following test:

Exp. 42: Taken, 0·2054 M_2O_5, 0·0512 Fe_2O_3. *HP*: 0·2014.

The fusion product was re-melted with strong sulphuric acid (5 c.c.), the mass disintegrated with water (400 c.c.), and about 25 c.c. of strong sulphurous acid added; this caused decided flocculation. The liquid was heated just to boiling, and filtered. The weighed hydrolysis precipitate (which was quite white) was fused with bisulphate, the product dissolved in tartaric acid, and the iron precipitated in the ammoniacal solution as sulphide which was ignited to Fe_2O_3; found, 0·0010 grm.

The earth-acid recovery is low; the absolute quantity of iron in the precipitate is small, though, relatively to the small amount taken, the proportion adsorbed is by no means negligible. Still, the separation by this method is an improvement over ordinary hydrolysis, and should give serviceable results with longer boiling and re-treatment of the precipitate.

We may dismiss the subject of the iron and earth acid separation with the remark that precipitation of the iron as sulphide from the ammoniacal tartrate solution is a reliable method (*cf.* Pied, ANALYST, 1925, **50**, 36).

CONCLUSIONS.—Having submitted our evidence, we will now venture a few conclusions:—(1) We have shown that, though the hydrolytic precipitation of the earth acids is not disturbed by zirconium, this element contaminates the precipitate to such an extent that the procedure cannot pass muster as a method of separation. The same applies, though to a less degree, to ferric iron and, no doubt, to other sesquioxides. The more stable salts of protoxides (iron, manganese, &c.) undergo slight, yet appreciable, adsorption. (2) The effect of association of titania with the earth acids in the hydrolysis was investigated quantitatively, and was found to be very marked at all intermediate stages preceding total precipitation of the mixed metallic acids, the titania and earth acid being more or less evenly distributed in the precipitate and in the solution. Association of zirconium with titanium causes the latter to react abnormally, *i.e.* not to be precipitated. The precipitation of the earth acids is impeded when they are in association with zirconia as well as titania. (3) The hydroxides of certain elements occurring in earth-acid minerals (tungstic, stannic, and antimonic acids) are insoluble under the conditions of the pyrosulphate-hydrolysis method; they are therefore included in the hydrolysis precipitate, and their removal therefrom by the accepted methods is ineffective (Sect. VIII, *loc. cit.*). (4) As a result of these observations, we have formed the opinion that the procedure cannot be described as a process of separation of the earth acids from their mineral associates; it is a precipitation method, and a very poor one at that, being, not a definite stoichiometric interchange, but a balanced reaction in which a colloidal phase gradually flocculates, with simultaneous adsorption of almost any of the constituents of the solution; filtration and washing of the precipitate are tedious; and complete precipitation of the earth acids cannot be ascertained by any simple or rapid test. (5) It may be objected that we have not studied the process by varying the relative proportions of the oxides to be separated, and that it furnishes a means of separating, *e.g.* small quantities of basic oxides from much earth acid. We are not prepared to dispute this altogether, though in such cases a small absolute error may still represent a considerable relative error; but our work has proceeded far enough to confirm our growing suspicion that the procedure is analytically unsound, and it should therefore be discarded as soon as a better scheme is available.

Such a scheme is the goal which we, together with our other collaborators, hope ultimately to attain, by working out with all necessary detail the pyrosulphate-tartaric acid method of which a preliminary outline was sketched in Section I (*loc. cit.*). The most important subsequent addition to the proposed process is the precipitation of the earth acids from the tartaric solution, described in Section IX (ANALYST, 1927, **52**, 633); a more extended study of this reaction has been begun.

Finally, we may point out that the evolution in earth-acid analysis here forecast has its counterpart in the analytical chemistry of titanium. The oldest process for determining this element is the pyrosulphate hydrolysis method, the largely diluted solution being boiled for some hours at an acid concentration of about 0·5 per cent. Here the difficulties are similar to, but less pronounced than, those dealt with in this paper. More recently, accurate and more convenient methods have been elaborated, so that, to quote Thornton (*Titanium*, New York, 1927, p. 91), "in view of its many disadvantages, the process may now be considered practically obsolete." Hillebrand's opinion (*op. cit.*, p. 138) is to the same effect: "It is inexplicable that the old method . . . should still find adherents in any part of the world."

SUMMARY.—The pyrosulphate-hydrolysis method has been experimentally investigated, with the following results: (1) The procedure does not afford a quantitative separation of the earth acids from zirconia by any of the modifications tried; a decrease in the quantity of co-precipitated zirconia is achieved at the cost of slightly incomplete earth-acid precipitation. (2) The deportment of mixtures of earth acids and titania is such that no separation of any practical significance takes place at any stage preceding total precipitation. (3) Zirconia prevents the hydrolytic precipitation of titania, and of the earth acids, as well, when titania is also present. (4) The separation of the earth acids from ferric sulphate is not feasible; the separation from ferrous sulphate is very much better, but not perfect. (5) The conclusion reached is, that the procedure is not a separation process; it is a very indifferent precipitation method, subject to the above and other causes of error. It should fall into disuse as the field of earth-acid analysis becomes more thoroughly explored.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE, LONDON, E.C.3.

A New Precipitation Method for the Determination of Vanadium, and its Application to Steel Analysis.*

BY B. S. EVANS, Ph.D., F.I.C., AND S. G. CLARKE, B.Sc., A.I.C.

(*Read at the Meeting, May 2, 1928.*)

IN a previous paper (A. T. Etheridge, ANALYST, 1928, 423, and the authors he cites) it has been shown that an accurate determination of vanadium can be made by a method which depends on the successive elimination of the various constituent metals of a steel, leaving a solution of vanadium accompanied only by metals (manganese, aluminium, etc.) which do not interfere in the ordinary

---

* Communication from the Research Department, Woolwich.

permanganate titration. Although the inaccuracies of the older precipitation methods (criticised by Cain, *Bull. U.S. Bureau of Standards*, **1911**, **7**, **377**), as well as the disadvantages of Cain's precipitation process are overcome by avoiding precipitation altogether, nevertheless the process (Etheridge, *loc. cit.*) requires some time to perform (3 days), and also, in the case of tungsten steels, it is necessary to recover vanadium from the tungstic oxide, which is filtered off from the steel solution. The process described below, in addition to materially shortening the time required, has also been applied to the determination of amounts lower than have previously been attempted. The inherent difficulty has been to find, among the numerous reactions of vanadium, one which is specific and which can be used for its direct determination in presence of the metals accompanying it in alloy steels.*

It seemed to the authors that a simpler method for the determination of vanadium in steel could be developed if it were possible to separate this element by direct precipitation from the steel solution, and in a form lending itself easily to subsequent determination. As, however, there is at present no satisfactory method of precipitating vanadium alone in presence of simple iron salts, which constitute the major product when a steel is dissolved in acids, the idea occurred of converting the iron into a complex form in which its ordinary reactions would not be displayed. The ferrocyanide ion was found most convenient in this respect, and it was at first hoped that vanadium would now be directly precipitable by cupferron. (This reagent, as is well known, precipitates vanadium alone from a weakly acid solution containing most of the "alloy" elements present in steel, but iron is quantitatively thrown down.) Experiment showed, however, that the brown cupferron-vanadium complex did not make its appearance in presence of ferrocyanide in slightly acid solution; instead, a greenish-brown precipitate separated. This was filtered off, ashed, and the vanadium determined by the method used in the process described below. A correct result was obtained. Further work showed that cupferron had played no part in this precipitation; it became evident that a ferrocyanide of vanadium was produced under these circumstances, and that it was a means of quantitative separation of vanadium from solution.

This precipitation method was subjected to a somewhat detailed investigation, with a view to discovering its applicability in presence of considerable amounts of metals now largely used as "alloying" elements in special steels, *e.g.* tungsten, chromium, nickel, etc., as well as the incidental metals in steel, *e.g.* manganese. During the course of this research, what is apparently a new reaction of iron was found, namely, its quantitative conversion from the ferric state in alkaline citrate solution, in presence of a cyanide and a reducing agent, *e.g.* sodium sulphite, into ferrocyanide; this is utilised in the process to be described.

So far as has been ascertained, very little is known of the ferrocyanides of vanadium and of some of the metals with which it is associated in special steels.

---

* An excellent review of the literature is given in "Analytical Methods for Certain Metals," by R. B. Moore and his collaborators. (Washington, 1923.)

What papers there are on this subject date from more than fifty years ago. Wyrouboff (*J. Chem. Soc.*, Abst., 1877, 190) describes vanadium ferrocyanide as a clear green bulky precipitate, and gives its formula as $(K_{18}V)[Fe(CN)_6]_6$; this he regards as somewhat doubtful, owing to his difficulty in obtaining an exact determination of vanadium. He also states that vanadium ferrocyanide is somewhat soluble in water, a conclusion which is scarcely justified, having regard to the present work. His work has been criticised, however, by Atterberg (*Ber.*, 1876, 9, 1475), who points to its general inaccuracy, and who gives the composition of this compound as $(5VO, K_6)\ [Fe(CN)_6]_4.60\ H_2O$ (Hoffmann, Lexicon der Anorg. Verb., 1914, II); no details of preparation or analysis could be ascertained, owing to the original paper being in Swedish, but the value for the water of hydration given should be taken with some reserve, as the precipitate is of a rather gelatinous nature, resembling in this respect ferric hydroxide. For this reason, and from the fact that it certainly adsorbs potassium ferrocyanide, we have made no attempt to determine its composition. This early work is merely of passing interest; no mention is made therein of the analytical significance of this valuable compound of vanadium.

Vanadium ferrocyanide separates, shortly after mixing an acid solution of vanadium and a soluble ferrocyanide, as a straw-yellow flocculent precipitate, which, when collected upon a filter, appears brownish. Its most outstanding property is that of insolubility in mineral acids of quite high concentration; results are quoted of experiments in which a few mgrms. of vanadium contained in a volume of about 400 c.c. were recovered by precipitation with potassium ferrocyanide at an acid concentration of over 12 per cent. by volume of sulphuric acid (beyond this strength the ferrocyanide ion itself begins to be attacked, as shown by the somewhat blue colour of the solution). It is soluble in alkaline media. It was found that organic acids, *e.g.* citric and tartaric acids, retard, or even prevent, the precipitation of vanadium ferrocyanide, but that their effect could be completely overcome by the addition of mineral acid in sufficient quantity; acetic acid is ineffective in this respect, although its use leads to quantitative precipitation in absence of interfering organic acids. It should be mentioned that precipitation by this method is carried out at the ordinary temperature; at higher temperatures the filtration properties of the compound are impaired; when the solution is boiled a large precipitate of indefinite composition is thrown down, and hydrocyanic acid is evolved. Vanadium ferrocyanide is unique in that it is almost the only form in which vanadium can be quantitatively precipitated in presence of fairly considerable amounts of acid, a property which may have applications outside the scope of this paper. Other points in connection with this precipitation, and the methods of final estimation of the vanadium, appear in the following description of the method worked out to provide an accurate determination of vanadium in steel:

DETERMINATION IN STEEL.—A five grm. sample of the steel is weighed into a 750 c.c. conical flask, 80 c.c. of dilute sulphuric acid (1: 7) are added, and the whole heated. When as much as possible has dissolved, sufficient nitric acid (approx. 5 c.c.) is added to clear up the carbonaceous residue; in the case of molybdenum steels, digestion for some time at a moderate temperature is necessary to yield complete solution, and in that of tungsten steels, to produce pure yellow tungstic oxide. Seventy c.c. of a strong solution of citric acid (100 grms. in 200 c.c.) are now added, followed by sufficient of a hot concentrated solution of sodium carbonate to render the solution neutral or *faintly* alkaline to litmus paper. Care must be observed not to make the solution *distinctly* alkaline, otherwise trouble may ensue in the next stage through ferric hydroxide separating from the solution. Cold saturated sodium carbonate should not be used, as it results in the steel solution becoming unduly dilute.

Any tungstic oxide will now have dissolved; in fact, a perfectly clear solution should be produced, whatever the composition of the steel.*

Nickel, if present, must now be separated. About 1 grm. of dimethylglyoxime, dissolved in a small quantity of hot alcohol, is added to the solution, which is then shaken and set aside over a steam bath for a few minutes, after which the red nickel precipitate is filtered off on a large rapid filter paper (No. 41 Whatman) and washed with hot water. (If the percentage of nickel present is greater than 4 or 5, more glyoxime must be used.) Failure to separate nickel will result in the production, later in the process, of an unfilterable precipitate of nickel ferrocyanide. In the absence of nickel, this addition of glyoxime should be omitted.

The solution is cooled down somewhat, and to it are added 25 grms. of sodium sulphite crystals, followed by a solution of 40–45 grm. of potassium cyanide in about 100 c.c. of water. Commercial cyanide is used, and, as it is generally obtained in the form of fairly large lumps, solution is obtained by gentle heating (not boiling, as this is liable to lead to some decomposition); before use, the solution is cooled. The contents of the flask are shaken for a short while to dissolve completely the sodium sulphite; meanwhile a rise of temperature occurs in the solution, and, in the case of a steel free from chromium and nickel, the deep red colour, produced when the cyanide is added, begins to bleach.† The flask is now placed over a source of heat, the solution maintained at a temperature somewhat below boiling for about 10 minutes and then actually boiled for about 5 minutes. The whole of the iron should now be in the form of ferrocyanide; as the success of the process depends very largely on this being so, the solution must be tested at this stage; a few c.c. are withdrawn into a small beaker and acidified with dilute sulphuric acid; if a Prussian blue colour develops, conversion of the iron into ferrocyanide has been incomplete, and the solution must be given a further boiling until a test shows no distinct blue colour. If necessary, a little more cyanide must be added. (After the test portions have been made slightly alkaline with sodium carbonate they are returned to the main solution.) The solution is now cooled until it is only slightly warm. In general, a brownish white precipitate will have separated

---

* Except a high silicon steel.

† When nickel has previously been separated by dimethylglyoxime, the red colour of the solution persists, even after complete conversion of the iron. The pure ferrocyanide colour is never attained in presence of chromium.

during the conversion of the iron; it consists of manganese ferrocyanide, and should not be filtered off, as it carries down some vanadium.

Dilute sulphuric acid (1: 3) is next added to the cooled solution until it is approximately neutral to litmus, followed by 70 c.c. in excess, added carefully, because much effervescence occurs. The solution is well shaken to free it as far as possible from gas and set aside for the precipitate of vanadium ferrocyanide to settle out. Our general practice is to allow it to stand overnight, but in the case of the ordinary amounts of vanadium found in steel it has been found quite accurate to filter after about two hours from the time of acidification. The solution is filtered on a rather large "free-running" pulp filter (*i.e.* one that has not been pressed down to any extent), care being observed to pour as much as possible of the supernatant liquid through the filter before disturbing the precipitate; it is washed with 2 per cent. ammonium nitrate. If the filtrate does not appear quite clear, it must be refiltered; this, however, is not a common necessity.

After being transferred to a platinum dish, the filter and precipitate are completely ashed at a moderate temperature, and this is followed by fusion with sufficient of a mixture of approximately 1 part of sodium phosphate and 5 parts of fusion mixture.* The melt (which is coloured green, due to manganese precipitated as ferrocyanide) is extracted with hot water and filtered into a small conical flask; washing is done, preferably, with dilute sodium sulphate solution, otherwise iron oxide shows a slight tendency to run through the filter. The filtrate is acidified with sulphuric acid, about 5 per cent. (1: 3) being added in excess, and is given a preliminary oxidation by boiling with a few drops of saturated solution of permanganate. After the addition of a few pieces of broken unglazed porcelain to ensure steady boiling, about 20 c.c. of saturated sulphur dioxide solution are added, and the liquid is boiled for 20 minutes and finally titrated with 0·1 *N* permanganate at 80° C.

The process does not require the separation of any elements other than nickel, as they do not cause any interference. This is especially significant in the case of tungsten, as apparently all processes heretofore described have required the separation of tungstic oxide which, as is well known, carries down with it notable amounts of vanadium, thus entailing further separations.

The above procedure gives accurate results for vanadium in any steel likely to be met with, down to the limit of the permanganate titration, *i.e.* a burette reading of about 1 c.c. of 0·1 *N* solution (corresponding to about 0·1 per cent. of vanadium on a 5 grm. sample). Below this amount (*e.g.* about 0·005 grm.), our experience is that the permanganate titration begins to fall off in accuracy as a measure of the vanadium, and no advantage seems to be gained by the use of 0·01 *N* permanganate solutions, in spite of the statements of some authors (*cf.* Cain and Hostetter, No. 8, *Tech. Papers, U.S. Bureau of Standards,* 1912). Fortunately this lower limit corresponds to the point below which amounts of vanadium cease to be interesting for most practical purposes.

---

* Admixture of sodium phosphate with fusion mixture has been found necessary to prevent manganese retaining part of the co-precipitated vanadium when the fused mass is extracted with water.

SMALL AMOUNTS OF VANADIUM.—In order to complete the scope of the method we have investigated the separation of quantities of vanadium of the order of a few mgrms. from a sample weight of 5 grms. (representing a few hundredths per cent.). It is, perhaps, realised that there are few methods extant whereby this may be done with reasonable accuracy combined with convenience in the case, say, of a high chrome-tungsten steel. Slight modifications are necessary in the main process when it is to be applied to the determination of these small amounts. In the first place the hydrogen peroxide method is used, both on account of accuracy and also, at the same time, to obtain a positive indication of the presence or absence of vanadium, which must finally be determined by a colorimetric process. In this connection it must be remembered that the fusion extract of the ferrocyanide precipitate is likely to contain certain other elements derived from the steel, *e.g.* molybdenum, which interfere in this colorimetric method, and must be removed prior to its application.

Secondly, it has been found that some constituents of special steels exercise a slight, but notable, interference with the precipitation of vanadium as ferrocyanide when the amounts of this element are low (under about 0·1 per cent. on a 5 grm. sample); this point is dealt with later.

When, therefore, traces of vanadium in steels are to be determined, the following procedure is recommended:

Method.—A 5 grm. quantity is dissolved, as far as possible, in dilute sulphuric acid (10 c.c. concentrated acid, 70 c.c. water), and oxidised with 5 to 10 c.c. of nitric acid, heating being continued until any tungsten has been converted to pure yellow tungstic oxide. This is filtered off, washed with dilute sulphuric acid and rejected,* and the filtrate treated exactly as described in the main process, with the one exception that, after the conversion into ferrocyanide, the liquid is acidified with 150 to 200 c.c. of 1 : 3 sulphuric acid instead of 70 c.c. After standing overnight it is filtered on a pulp filter which has been pressed down fairly tightly, thoroughly washed with 2 per cent. sulphuric acid, ignited, fused and extracted as before. The fusion extract is concentrated to about 60 c.c., cooled, 20 c.c. of concentrated sulphuric acid added, and the solution, which is now hot owing to the addition of the acid, is treated with a few drops of dilute permanganate solution to give it a faint pink colour; this makes certain that the vanadium exists in the pentavalent condition. The solution is cooled, transferred to a 100 c.c. Nessler glass, and hydrogen peroxide added, drop by drop, with stirring, until the depth of colour reached is at a maximum;† 0·5 c.c. of 3 per cent. solution is usually amply sufficient; liberal excess is dangerous, as it has a bleaching effect. The colour produced is matched by running a standard solution of ammonium vanadate (0·0010 grm. of vanadium per c.c.) into a similar Nessler glass containing 15 to 20 per cent. sulphuric acid and hydrogen peroxide.

If titanium is suspected, a drop of hydrofluoric acid (no more) is added to the

---

* In the special case here considered the amount of vanadium is too small for the adsorption on the tungstic oxide to have any significance.

† Meyer and Pawletta (*Z. anal. Chem.*, 1926, **69**, 19) recommend 1 drop only.

colorimetric solution to bleach any colour due to this element. With high chromium steels a slight greenish tint may sometimes be noticed in the peroxidised solution, owing to the difficulty of washing the ferrocyanide precipitate entirely free from chromium; the amount, however, is insufficient to interfere seriously with the colorimetric process. If it is greater, through some accidental cause, the chromium must be removed either by a caustic soda separation, or, preferably, by precipitating the vanadium with cupferron* in the cold solution, after boiling to decompose hydrogen peroxide and neutralising most of the sulphuric acid; the precipitate is filtered off after a few minutes, washed with a very dilute slightly acid solution of cupferron, ignited, fused with fusion mixture, and the vanadium determined, as before, in the extract from this fusion.

Molybdenum is the only element requiring special consideration in this method for small amounts of vanadium. When it is present, 10 grms. of sodium fluoride should be dissolved in the solution before the precipitation of vanadium ferrocyanide by the addition of acid (ordinary laboratory resistance glass is scarcely attacked, if at all, at the concentration of fluoride represented by this addition). The molybdenum which accompanies vanadium in the ferrocyanide precipitate must be removed before the colorimetric determination of vanadium is attempted, by precipitation as sulphide in slightly acid solution, with the usual precautions, as molybdenum yields a yellowish brown colour with hydrogen peroxide.

TESTS OF THE PROCESS.—The process was tested, in the first place, on plain steels and "Armco" iron, to the solution of which in the stated amount of acid were added various amounts of metallic salts and standard vanadium solution to simulate any desired steel. In some cases the proportions do not correspond to any known class of steel, but represent rather extreme cases; the results are given, however, to show the wide range of applicability of the method. Later, several vanadium steels which had already been analysed by reliable independent methods, including certain British Chemical Standard steels, were submitted to the process described. (Table III.) Results obtained with amounts of vanadium coming within the applicability of the permanganate titration are first given, *i.e.* the percentages usually found in vanadium steels. The work was planned on the use of a 5 grm. sample. In some cases plain or alloy vanadium-free steel of about 0·5 per cent. manganese content was used in the experiments, otherwise "Armco" iron was taken; both are referred to indiscriminately as "steel" in the tables.

TABLE I. PLAIN STEEL.

	Taken. Steel.	Added. Vanadium.		Required. $N/10$ $KMnO_4$.	Found. Vanadium.	
	Grms.	Grm.	Per Cent.	c.c.	Grm.	Per Cent.
i.	5·0	0·0502	1·00	9·85	0·0502	1·00
ii.	5·0	0·0497	0·99	9·70	0·0495	0·99
iii.	5·0	0·0204	0·41	3·95	0·0201	0·40
iv.	5·0	0·0253	0·51	5·00	0·0255	0·51
v.	5·0	0·0100	0·20	2·00	0·0102	0·20
vi.	5·0	0·0050	0·10	0·95	0·0048	0·10

---

* For further details see *J. Ind. Eng. Chem.*, 1920, **12**, 344.

TABLE II. ALLOY STEELS.

	Taken. Steel.	Added. Vanadium.			Other metals.		Required. $N/10$ $KMnO_4$.	Found. Vanadium.	
	Grms.	Grm.	Per Cent.		Grm.	Per Cent.	c.c.	Grm.	Per Cent.
i.	4·0	0·0500	1·00	Cr	1·0	20	9·75	0·0497	0·99
ii.	4·0	0·0250	0·50	Cr	1·0	20	4·85	0·0247	0·49
iii.	4·0	0·0050	0·10	Cr	1·0	20	1·05	0·0054	0·11
iv.	3·0	0·0050	0·10	Cr W	1·0 1·0	20 20	1·00	0·0051	0·10
v.	4·0	0·0500	1·00	W	1·0	20	9·55	0·0487	0·97
vi.	4·0	0·0250	0·50	W	1·0	20	4·90	0·0250	0·50
vii.	5·0	0·0250	0·50	Mo		1	4·80	0·0245	0·49
viii.	5·0	0·0250	0·50	Ni		6·97	4·95	0·0252	0·50

TABLE III.

	Steel.	Percentage composition. Mn.	Ni.	Cr.	Co.	W.	Vanadium found. Independent process.*	This process.
i.	B.C.S. "V" (nominal ·273 per cent. V)	0·542	—	0·861	—	—		0·30
ii.	B.C.S. "W" (nominal ·791 per cent. V)	0·101	0·44	3·01	4·76	16·21		0·78
iii.	Nickel-chromium	0·58	2·9	1·4			0·18	0·18
iv.	Nickel-chromium	—	3·4	0·9			0·25	0·24

SMALL AMOUNTS OF VANADIUM IN STEEL.—The following results were obtained by the modified process described:

TABLE IV.

	Taken. Steel.	Vanadium.			Added (or present). Other metals.		Found. Vanadium.	
	Grms.	Grm.	Per Cent.		Grm.	Per Cent.	Grm.	Per Cent.
i.	5·0	0·0020	0·04		None exc. Mn, traces Cu, etc.		0·0020	0·04
ii.	5·0	0·0010	0·02		None exc. Mn, etc.		0·0012	0·02
iii.	5·0	0·0020	0·04		None exc. Mn, etc.		0·0020	0·04
iv.	4·75	0·0010	0·02	Ni	0·25	5·0	0·0009	0·02
v.	5·0–Ni	0·0020	0·04	Ni Mn	—	6·97 0·80	0·0020	0·04
vi.	4·0	0·0020	0·04	W	1·0	20	0·0018	0·04
vii.	3·0	0·0010	0·02	W Cr	1·0 1·0	20 20	0·0008	0·02
viii.	5·0	0·0050	0·10		as in (i.)		0·0048	0·10
ix.	5·0	0·0005	0·01		as in (i.)		0·0006	0·01
x.	5·0–Ni–Cr–Mo	0·0020	0·04	Cr Ni Mo		1·34 4·74 1·08	0·0017	0·03
xi.	3·0	0·0020	0·04	W Cr	1·0 1·0	20 20	0·0017	0·03
xii.	4·0	0·0010	0·02	Cr	1·0	20	0·0010	0·02
xiii.	4·0	0·0020	0·04	Cr	1·0	20	0·0018	0·04

There are certain points of chemical interest in connection with the process described.

CONVERSION OF FERRIC SALTS INTO FERROCYANIDE.—Before the procedure incorporated in the process was devised a troublesome method was used, depending

---

* Etheridge, ANALYST, 1928, 423.

on the reduction of the iron with sulphur dioxide and subsequent addition of excess of alkali and potassium cyanide. Conversion by this means was never complete, since it is practically impossible to reduce 5 grms. of iron from the ferric to the ferrous condition, owing to the fact that it is essential that the solution must be very nearly neutral for complete reduction; this makes frequent re-neutralisation necessary, during the course of the reduction, of acid liberated in the reaction. Furthermore, slight oxidation invariably resulted on adding alkali and cyanide. On account of this, when the solution was subsequently acidified, variable, though often considerable, amounts of Prussian blue were precipitated, rendering filtration of the solution almost impossible.

Considering the strong tendency which exists for the formation of ferrocyanide in alkaline solution from a ferrous compound and potassium cyanide, the possibility was explored of converting a ferric salt into ferrocyanide by reducing it, while held in alkaline solution by a citrate in presence of cyanide. This method proved entirely successful with several reducing agents tried. With sodium hydrosulphite, $Na_2S_2O_4$, conversion from the ferric state to ferrocyanide proceeded to completion at temperatures only slightly above the ordinary; but with sodium sulphite just below the boiling point; and similarly with glucose. Many metallic reducing agents produced some ferrocyanide, but not so readily. Indeed, by boiling an alkaline citrate and ferric solution with potassium cyanide alone, complete conversion of the iron into potassium ferrocyanide may be effected, but a considerable excess of this reagent has to be added, as some is used in reducing iron to the ferrous condition; with the reducing agents mentioned, conversion is complete with almost the theoretical amount of potassium cyanide, according to the equation:

$$2Fe(OH)_3 + 12KCN + Na_2SO_3 \longrightarrow 2K_4Fe(CN)_6 + 4KOH + Na_2SO_4 + H_2O.$$

In calculating the amount of potassium cyanide to be used for 5 grms. of iron, allowance must be made for the fact that the commercial salt rarely exceeds about 90 per cent. purity; hence 40 to 45 grms. are recommended instead of the theoretical amount of approximately 35 grms. With highly alloyed steels containing less iron this quantity of cyanide may be reduced proportionately; no error, however, is introduced through keeping to the stated amount; experiments which have been carried out show that excess of cyanide is without influence on the results.

It has been found that a considerable excess of sodium sulphite (provided for in the process) over the calculated quantity is necessary for complete reduction and conversion into ferrocyanide.

In connection with reducing agents used in the investigation it should be mentioned that sodium hydrosulphite, although quite satisfactory when used with plain steels, gave anomalous results when applied in the case of high chromium steels; for a reason as yet unknown the precipitation of vanadium ferrocyanide was completely prevented when this reagent had been used in the conversion of iron into ferrocyanide. Its general use was abandoned.

Another perplexing fact encountered in the work arose from the use of ammonia in the process instead of sodium carbonate; bad results were obtained with high chromium steels, occasioned, perhaps, by the formation of a stable soluble chromium and vanadium ammine complex, or, possibly, the production of some condition under which vanadium ferrocyanide is "peptised." The difficulty was completely overcome by the use of sodium carbonate in the process.

CONDITIONS OF ACIDITY FOR PRECIPITATING VANADIUM FERROCYANIDE.—In amplification of remarks in the introductory section some results are quoted of experiments carried out with a view to establishing the acidity conditions for precipitating small amounts of vanadium in the ferrocyanide process.

(*a*) *Precipitation of Vanadium alone.*—Small known amounts of vanadium were added to an alkaline solution of 10 grms. of potassium ferrocyanide to which had been added 70 c.c. of citric acid solution (the quantity employed in the analytical process). The solution was neutralised, the specified excess of sulphuric acid added, and the volume adjusted to approximately 400 c.c. It was allowed to stand overnight before filtering; the vanadium precipitated was determined as already described.

TABLE V.

	Added. Vanadium. Grm.	Excess. H_2SO_4 (1 : 3) c.c.	Found. Vanadium. Grm.
i.	0·0020	25	0·0020
ii.	0·0020	50	0·0019
iii.	0·0020	100	0·0020
iv.	0·0020	200	0·0020
With 30 grm. tartaric acid instead of citric acid as above:			
v.	0·0020	50	0·0020
vi.	0·0020	100	0·0020

"Armco" iron was submitted to the process described, small amounts of vanadium having been added; the final acidification was effected with the volumes of sulphuric acid specified:

TABLE VI.

Taken Armco iron. Grms.	Added. Vanadium. Grm.	Excess. H_2SO_4 (1 : 3) c.c.	Found. Vanadium. Grm.
5·0	nil	150	nil
5·0	0·0020	70	0·0019
5·0	0·0020	100	0·0019
5·0	0·0020	200	0·0019

(*b*) *Precipitation in Presence of Chromium.*—The following results were obtained in presence of 20 per cent. of chromium:

TABLE VII.

	Taken. Armco iron. Grms.	Vanadium. Grm.	Added. Chromium. Grm.	Excess. H_2SO_4 (1 : 3) c.c.	Found. Vanadium. Grm.
(1)	4·0	0·0010	1·0	100	0·0007
(2)	4·0	0·0020	1·0	100	0·0015
(3)	4·0	0·0010	1·0	200	0·0010
(4)	4·0	0·0020	1·0	200	0·0018

These results illustrate the necessity of high acidity in the case of chromium, low vanadium, steels.

The following is a summary of the behaviour of the metals likely to be met with in this ferrocyanide method for vanadium:

Chromium does not precipitate under the conditions of the process and does not interfere. In the case of high chromium steels, a small amount is adsorbed on the ferrocyanide precipitate, but this is not sufficient to have any influence on the permanganate titration, as has been proved experimentally. With traces of vanadium, increase in the acidity for precipitation (provided for in the process and illustrated in (3) and (4) in Table VII) yields satisfactory results.

Nickel produces an unfilterable precipitate of nickel ferrocyanide in the process, and must be separated as indicated.

Cobalt.—No interference was noted in the analysis of the cobalt steel recorded in Table III (ii).

Tungsten does not precipitate in the determination of ordinary amounts. When dealing, however, with traces of vanadium in high tungsten steels, the tungsten must be previously separated as trioxide; otherwise, with the high acidity used for precipitation of vanadium, it has a tendency to cause low results.

Copper will, of course, precipitate almost completely with the vanadium. No interference is produced by the small amounts present in steels. As an actual constituent it has not been dealt with in this paper, on account of its rarity.

Manganese accompanies vanadium in the ferrocyanide precipitate, and comes down in a rather powdery form; it does not interfere. It may be quantitatively determined by the process described for vanadium, if the ignited ferrocyanide precipitate is fused with potassium pyrosulphate, extracted with water, and this solution submitted to the bismuthate process for manganese. For example, 4·4 grms. of a plain steel gave: manganese, 0·740 per cent.; found by a reliable independent method, manganese, 0·735 per cent.

Molybdenum precipitates with the vanadium, whether quantitatively or not, has not yet been ascertained. It does not interfere in the permanganate titration of vanadium as described, but it must be removed before applying the hydrogen peroxide colorimetric method for vanadium.

Titanium precipitates as ferrocyanide, but is eliminated as insoluble sodium titanate in the fusion of the ferrocyanide precipitate. Small amounts present in a steel, which may yet escape removal in this way, do not affect the permanganate titration as used in the process, and have no influence on the colorimetric method in presence of a small quantity of hydrofluoric acid.

DISCUSSION.

DR. SCHOELLER said that he fully realised the difficulty of the problem the authors had set out to solve when they addressed themselves to the determination of vanadium in special steels containing several interfering elements. He invited the authors to make comparative tests with Roesch and Werz's method, an abstract of which would shortly appear in the ANALYST, and which to him seemed likely to combine reasonable accuracy with comparative simplicity. In it the vanadium was brought into solution by fusion with sodium hydroxide, and titrated iodimetrically in presence of an excess of phosphoric acid, reduction proceeding only to the tetroxide stage.

DR. B. S. EVANS, in reply, said that they had not had time to try Roesch and Werz's method; judging from the abstract, however, he doubted whether the method, as applied to steel analysis, would be quite as simple as it looked at first sight. For instance, the authors mentioned "filtering off any tungstic acid," but they gave no indication of how one was to recover the vanadium which was co-precipitated with it; also their method required an ether separation of the iron, a somewhat tedious and wasteful process, the avoidance of which the authors of the present paper claimed as one of the special merits of their process. He thought, also, that in the presence of much chromium the filtering and washing of the manganese vanadate precipitate might be a tiresome operation.

The Determination of Carbon Dioxide in Carbonates in Soil.

BY A. RIAD, Ph.D., B.Sc.

(*Read at the Meeting, April 4, 1928.*)

HEPBURN'S modification (ANALYST, 1926, **51**, 622) of the Van Slyke method of determining carbon dioxide in carbonates affords a simple and accurate substitute for the tedious or inaccurate methods of Fresenius and Classen, Schrötter, Pettersson, and Lunge and Marchlewski. The error in the results quoted in Hepburn's paper ranges from about 0·15 to 1·4 per cent. of the theoretical value for the carbon dioxide.

At the suggestion of Mr. W. S. Gray, Director of the Chemical Section, Ministry of Agriculture, Egypt, I have tested the method, with a view to adapting it for use in the analysis of soils.

In the course of the experimental work the following observations were made:

In introducing the baryta into the flask a part of it is undoubtedly used up by the carbon dioxide of the atmosphere, especially if the baryta is run in slowly from a burette, with consequent exposure of a large surface to the air for a comparatively appreciable period. An obvious modification consists in passing a slow current of air into the flask through a soda-lime tube for half-an-hour before introducing the baryta. Also, every precaution should be taken to minimise the period of contact between the baryta and the atmospheric air throughout the different stages of the process. To carry out the titration as quickly as possible, the oxalic acid should be run into the remaining baryta quickly and without regard to an end-point. The excess acid is then back-titrated against the standard baryta.

Again, it was found that reducing the pressure to 6 or even 7 cm. of mercury answers the purpose just as well as reduction to 2 cm.

The method was first tried on a pure sample of anhydrous sodium carbonate, with the following results:

Taken. Grm.	Found. Grm.	Error. Per cent.
0·2049	0·2029	−1·00
0·1744	0·1736	−0·45
0·3042	0·3026	−0·52

A sample of an average clay soil was next treated with warm* dilute hydrochloric acid for a few hours and left overnight in contact with the acid. The next morning the soil was filtered off, thoroughly washed with hot water, dried in the steam oven for two hours, and cooled in a desiccator containing a dish of fresh sodium hydroxide powder. Small amounts of pure anhydrous sodium carbonate were accurately weighed and mixed well with approximately 4 to 5 grms. of the soil, and the carbon dioxide determined. The following results were obtained:

Sodium carbonate, added, grm.:	0·1092	0·0542	0·1236	0·0677	0·1020	0·0899	0·0967
Sodium carbonate, found, grm.:	0·1082	0·0544	0·1240	0·0680	0·1024	0·0902	0·0971
Error, per cent.	−1·00	+0·37	+0·32	+0·44	+0·39	+0·33	+0·41

CHEMICAL LABORATORY,
MINISTRY OF HEALTH, EGYPT.

DISCUSSION.

Dr. J. A. VOELCKER asked in what respect the method showed any superiority over that of Collins (calcimeter method), which was very accurate, and much more expeditious, seeing that a determination occupied only about ten minutes. He had ascertained on enquiry that the calcimeter method was exclusively used in the Rothamsted soil laboratory and was found to be very satisfactory.

---

* Treating the soil in the cold is not sufficient, as it was proved that the soil still contained carbonates, even after standing for 10 hours with the acid.

Seasonal Variations in the Composition of the Latex of *Hevea brasiliensis*.—*Erratum:* On p. 331 it is stated that the P_H value is 6·5, and that this is alkaline to methyl orange and to phenolphthalein. This should read "alkaline to methyl orange, but acid to phenolphthalein."

Notes.

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

WATER IN CREAM.

WHILE working on the subject of glycerin in cream, it was at first thought that if the sample contained the normal proportion of solids-not-fat it might be presumed that glycerin was absent. Looking more closely into the figures obtained on samples examined in this laboratory, however, I found that this method could be of no use, as nearly all the samples (not including sterilised or clotted cream) on which the amount of solids were determined were deficient in solids-not-fat.

The percentage of solids-not-fat in the serum of cream should not fall below 8·7 per cent. (cream from minimum milk), and for cream made from average milk the percentage is 9·2.

The following table gives a selection from figures obtained in this laboratory:

Sample.	Total solids. Per Cent.	Fat. Per Cent.	Solids-not-fats. Per Cent.	Solids-not-fat in serum. Per Cent.	Added water in serum. Per Cent.	Water added to original cream. Per Cent.
1.	54·7	51·2	3·5	7·2	17	8
2.	50·5	47	3·5	6·6	24	13
3.	57·0	54	3·0	6·5	25	11
4.	57·8	54	3·8	8·3	5	2
5.	49·9	48	1·9	3·7	57	30
6.	60·5	57·5	3·0	7·1	18	8
7.	36·2	30	6·2	8·9	made in laboratory.	
8.	52·9	48·5	4·4	8·6		

Out of 21 samples bought either as cream or preserved cream (but not sterilised or clotted),

19 samples contained less than 8·0 per cent. of solids-not-fat in serum.
18 ,, ,, ,, ,, 7·5 ,, ,, ,, ,, ,, ,,
13 ,, ,, ,, ,, 6·5 ,, ,, ,, ,, ,, ,,
8 ,, ,, ,, ,, 5·5 ,, ,, ,, ,, ,, ,,
2 ,, ,, ,, ,, 4·5 ,, ,, ,, ,, ,, ,,

It was a surprise to find that the bulk of the cream of (chiefly) local make contained added water. If cream, when nearly ready for sale, is too thick or hard, one would have thought that whole or separated milk would have been used for the thinning-down process. The dairymen, however, appear to prefer using water for this purpose, and, according to one from whom information was obtained, this preference is deliberate and is based on the fact or belief that a more satisfactory mixture is obtained with water than with milk. In the latter case, according to one man, the product is liable to become rather lumpy. Possibly this may sometimes be true, particularly when the cream has had time to ripen or is sour to any extent.

Two out of five dairymen readily admitted that it was customary to thin cream with water; the others denied it.

If a cream is sufficiently rich in fat, there does not seem much point in objecting to its being deficient of 1 or 2 per cent. of solids-not-fat. On the other hand, one can hardly approve of allowing the indiscriminate addition of water to a product like cream, especially as no fat standard is in existence.

Prosecutions for water in cream are few but not unknown (*cf.* ANALYST, 1910, **35**, 8, and *The Grocer*, May, 1910).

In 1920 the Food Controller issued the Milk Order, 1920 (No. 116) which, *inter alia*, forbade the addition of water or colouring matter to cream intended for sale. The Milk (England and Wales) Order, 1921, replaced this order, but repeated the above injunction. This second order was, in part, superseded by the Milk and Dairies (Amendment) Act, 1922 (Sec. 3), but is still theoretically in force, so far as it affects the addition of water or colouring matter to cream.

As far as can be gathered, the Order appears to have remained a dead letter throughout the country, but the situation seems unsatisfactory.

My thanks are due to the Birmingham City Analyst for permission to publish this note.

A. F. LERRIGO.

ANALYTICAL DEPARTMENT,
44, BROAD STREET, BIRMINGHAM.

Richmond (ANALYST, 1914, **39**, 246) has shown that the aldehyde figure of cream affords a rapid means of determining whether a cream has been watered. In his "*Dairy Chemistry*" (p. 187) he gives a formula which shows the average relationship between fat, solids-not-fat, and total solids in cream, and also a table in which the fat and solids-not-fat are calculated from the percentage of total solids; any deviation of solids-not-fat from the figures calculated either from the fat or total solids would indicate that the sample had been watered.—EDITOR.

THE DETERMINATION OF ADDED PHENOL AND CRESOL IN MILK.

DURING a recent clean milk competition a sample of milk was presented for examination, which had a bitter taste and sharp smell, suggestive of phenolic contamination. This was verified by the technique given below, while controls done on pure fresh milk gave no reaction.

The method employed was that given by Mumford (ANALYST, 1913, **38**, 336), and consisted in the conversion of the phenolic compound into ammonium picrate which was then determined colorimetrically by comparison with a standard ammonium picrate solution.

The technique can be conveniently applied to milk as follows:

(1) To 50 or 25 c.c. of milk, add cautiously, 2 c.c. of concentrated sulphuric acid to precipitate casein and sulphonate the phenolic compound present.

(2) Filter and wash, and heat the combined filtrate and washings to 85° C. in a waterbath for 10 minutes.

(3) Cool, and filter off the coagulated albumin.

(4) Add 5 c.c. of 10 per cent. potassium nitrate solution to the filtrate and heat to 80° or 90° C. to effect nitration.

(5) Filter, if necessary, cool to room temperature under the tap, and make alkaline with ammonia solution (sp. gr. 0·880). The yellow colour, due to the formation of ammonium picrate, is manifest at once, and can be measured colorimetrically by comparison with standards, made from pure phenol-sulphonic acid (B.D.H.), which has been similarly nitrated and converted into ammonium picrate. The milk under examination gave a colorimetric reading equivalent to 0·065 grm. of phenol per 100 c.c. of milk.

This technique was further investigated by treating a series of milk samples (50 c.c. each) with pure phenol in the dilutions stated below, and comparing the delicacy of the chemical test obtained with them, with the indications of phenolic contamination obtained by taste and smell.

The results were as follows:

Dilution.	Taste.	Smell.	Test.
1/100	+++	+++	+
1/1000	++	++	+
1/10,000	faintly +	doubtful +	+
1/100,000	—	doubtful	doubtful
1/1,000,000	—	—	—

It appears that taste and smell cannot detect phenol at greater dilution than 1/10,000, and that the chemical test compares favourably with both.

The reaction was found to be quantitative for additions of phenol ranging from 0·1 grm. to 0·005 grm. per 50 c.c. of milk. This experiment was repeated with cresols, but the test cannot be recommended for cresolic taints, since a satisfactory colour could not be obtained at dilutions below 0·1 grm. per 50 c.c. of milk.

H. T. Fawns.

The National Institute for Research in Dairying,
University of Reading.

Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

Report of the City Analyst for the Second Quarter, 1928.

Of the 1415 samples examined, 1235 were taken under the Food and Drugs Acts, 1167 being bought informally (78 adulterated), and 68 formally (16 adulterated).

Milk from Starved Cows.—Twenty samples from one farmer, taken at the railway station, on 8 occasions, between April 2 and May 31, gave results ranging from 3·1 to 3·75 per cent. for fat, and from 8·0 to 8·8 for solids-not-fat. A sample of evening milk taken from the cows contained 8·0 per cent. of solids-not-fat and 3·5 per cent. of fat. The report of a veterinary surgeon was to the effect that the animals were being starved. It is often alleged that a milk showing a considerable excess of water is due to starvation of the cows; but in this case, although the starvation appears to have been extreme, the milk was only 0·5 per cent. below the presumptive limit for solids-not-fat. In view of the case *Hunt* v. *Richardson*, there is no alternative to passing such milk as genuine milk.

INFUSION OF SENEGA.—Infusion of senega is required by the B.P. to be made by infusing one part of senega root in 20 parts of water. Twelve samples of the senega root were obtained and infusions made according to the B.P. directions. Eleven yielded infusions containing 1·14 to 1·48 per cent. of total solids, owing to the natural variation in the roots, some of which were of poor quality. The standard used (1·2 per cent. of total solids) was therefore a lenient one. The remaining sample yielded only 0·94 per cent. of solids, but the root from which it was made was at least 40 years old.

In ordinary dispensing practice the infusion is rarely freshly made, but one ounce of concentrated infusion is diluted to eight ounces with water. No serious objection can be made to this practice if the product closely resembles the infusion of senega prepared according to the British Pharmacopoeia.

A number of concentrated infusions of senega were examined, and the amount of total solids was found to vary from 2·9 to 10·5 per cent. To correspond with the standard for infusion of senega, taken above, at least 9·6 per cent. should be present.

It is not likely that the deficiencies in these concentrated infusions were due either to the variation in the composition of senega root or to decomposition, but it is impossible to say whether the low proportion of total solids found was due to a faulty method of manufacture or to the omission of part of the drug which should have been used. The B.P. infusion is prepared from senega and water only, but these concentrated infusions contained glycerin, spirit, chloroform or ammonia as preservatives (see also p. 499).

BORAX HONEY.—The B.P. requires 10 per cent. of borax to be present in this preparation, but an informal sample contained only 4·3 per cent. The vendor, when cautioned, attributed the deficiency to accidental admixture of honey with the borax honey. Five other samples were in reasonable agreement with the B.P. requirements.

METROPOLITAN BOROUGH OF STEPNEY.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1927.

DURING the year, 1347 samples were submitted, of which 1292 were taken under the Food and Drugs Acts, 884 being formal and 408 informal; 42 were adulterated.

LABELLING OF CREAM CHEESE.—Eleven samples were all found to be adulterated. Two samples labelled "Bondon" had the following percentage composition:

Water.	Fat.	Proteins.	Ash.	Fat in milk used. Calculated.
76·6	1·2	17·2	1·56	0·2
70·1	4·0	18·8	2·40	0·8

Although there is some difference of opinion as to whether "Bondon" cheese should be made from whole milk or skimmed milk, such a description gives no indication to the purchaser that only a negligible amount of milk fat is present.

I would suggest that soft cheeses should be described as follows:—(1) *Cream Cheese*, containing at least 35 per cent. of fat. (2) *Milk Cheese*, containing at least 15 per cent. of fat, and made either from whole or skimmed milk. (3) *Curd Cheese*, containing less than 15 per cent. of fat.

"Bondon" cheeses would of necessity be labelled under (2) or (3), and the use of the word would probably disappear.

DOUGLAS HENVILLE.

Legal Notes.

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

ARSENIC IN BAKING POWDER.

ON June 26 an action was tried before Judge Moore, at Southwark. The plaintiff, a baking-powder manufacturer, sued a firm of chemical manufacturers to recover £71 13s. 2d. damages for breach of contract for the sale of twenty 1 cwt. kegs of acid calcium phosphate which the defendants had expressly warranted to comply with the Food and Drugs Acts. The defendants denied that they had given any warranty, and contended that if any such warranty had been given the acid calcium phosphate complied with it. They had not manufactured the phosphate, but had sold it under a similar guarantee from the manufacturers. Further, they denied that the analysis made on behalf of the plaintiff was a correct analysis of their acid calcium phosphate, and they denied that the phosphate used by the plaintiff in his baking powder was supplied by them.

It was stated by counsel for the plaintiff that they supplied the plaintiff with 1 ton of acid calcium phosphate, and that he had mixed it with other ingredients to form baking powder. One of his customers, a grocer in Essex, had been prosecuted for selling baking powder containing an excess of arsenic, and had been fined £5 and £5 costs, which the plaintiff had paid. He had also been put to great expense in recovering the baking powder sent out to his customers. He had had no acid calcium phosphate on his premises other than that supplied by the defendants.

Dr. Bernard Dyer said that he had analysed a sample of baking powder received from an inspector, and had found it to contain 1/16 grain of arsenic per lb. In cross-examination, he said that sodium bicarbonate and rice flour, the other constituents of the baking powder, were very pure, and that therefore the arsenic must have come from the acid calcium phosphate. The recommendations of the Royal Commission on arsenic were not statutory, but they were accepted by analysts, the Courts, and the trade. The words of the Act were "as ordinarily used in food," and acid calcium phosphate was an ingredient used every day in food. He agreed that the British Pharmacopoeia allowed 5 parts per million of arsenic in neutral calcium phosphate, and that it might be described as a fine chemical. Legally speaking, he regarded acid calcium phosphate as a food. The recognised amount of arsenic allowed in baking powder was 1·4 parts per million.

Dr. H. E. Cox said that he had analysed samples of baking powder and acid calcium phosphate, and had found 1/14 grain of arsenic per lb. in the baking powder, or 9 parts per million, and 20 parts per million in the phosphate. He agreed with Dr. Dyer that the B.P. Codex fixed standards of purity, but that they applied to medicines and drugs, and not to foodstuffs.

Mr. E. J. Parry, F.I.C., said that he had analysed samples of the acid calcium phosphate used, and had found from 6 to 7 parts per million. As it was improbable that arsenic was present in the sodium bicarbonate, he concluded that it was not the same acid calcium phosphate as had been supplied to the plaintiff.

Counsel for the defendant submitted, that, taking 7 parts per million as an average of what three analysts had found in the acid calcium phosphate, which was a third of the baking powder, that would be 2·3 parts per million in the baking powder. Under Sec. 26 of the Sale of Food and Drugs Act, 1899, the words read "and any article which ordinarily enters into food," and he submitted that acid calcium phosphate could not be described as "ordinarily entering into food." It was an ingredient of an ingredient and was described as a fine chemical.

On July 16th Judge Moore gave his reserved judgment in the action. He found that the consignment of acid calcium phosphate delivered on September, 1927, was not of the nature, substance and quality demanded; in other words, that there had been a breach of warranty. He was satisfied that the baking powder which had been the subject of the prosecution in the Essex case had been made with acid calcium phosphate from the consignment referred to in the invoice, and it was clear from Dr. Dyer's evidence that that baking powder was contaminated with arsenic to the extent of about 9 parts per million. As it had been proved that it was improbable that the other ingredients could have been responsible for the contamination, it followed that the sample examined by Dr. Dyer must have been contaminated to the extent of about 27 parts per million. A portion of the sample of baking powder had been analysed by Dr. Cox, who had obtained practically the same result as Dr. Dyer. Dr. Cox had also analysed a sample of the acid calcium phosphate itself taken from the same consignment, and had found it to contain 20 parts of arsenic per million. This, although somewhat less than the 27 parts, calculated from Dr. Dyer's analysis of the baking powder, was admittedly far in excess of what was allowable, and the case against the defendant, therefore, was, he thought, complete.

Subsequently samples of the acid calcium phosphate had been analysed by Mr. Leo Taylor and by Mr. Parry, both of whom had obtained results very much more favourable to the defendants. He did not know what was the explanation of the discrepancy. Possibly the contamination was not evenly distributed throughout the bulk, or the whole consignment was not made at the same time. But whatever the explanation, he must hold that the contamination admitted—somewhere about 7 parts per million—was considerably greater than would be permissible. Upon the evidence he found that the outside permissible limit of contamination would be 4 parts per million in acid calcium phosphate, which would mean 1·4 parts per million in the baking powder, and that in practice the contamination was usually a good deal less. He held that the samples analysed by Dr. Dyer and by Dr. Cox were contaminated to a very much greater extent than 6 or 7 parts per million. It followed that the plaintiff was entitled to recover damages for breach of warranty. Judgment was entered for the plaintiff for the sum claimed and costs. An application for a stay of execution, with a view to an appeal, was allowed.

Department of Scientific and Industrial Research.

THE INVESTIGATION OF ATMOSPHERIC POLLUTION.*

REPORT ON OBSERVATIONS IN THE YEAR ENDING MARCH 31ST, 1927.

THE work of the Advisory Committee on Atmospheric Pollution has now been taken over by the Dept. of Scientific and Industrial Research, but the present, 13th, Report is made under the old organisation.

SECTION I. RESULTS OBTAINED BY DEPOSIT GAUGES.—*Standard Gauge.* The deposit of impurity at 80 stations is classified as in previous years (*cf.* ANALYST, 1927, **52**, 155), and the stations placed as A to D in order of quantity of impurity. From 1914 to 1927 the number of stations ranking as A and B has increased from 54 per cent. of the total to 87 per cent., but those ranking as D remain at 4 per cent. Highest and lowest figures, as metric tons per hundred square kilometres, for the year were:—*Tar,* Burnley, 939; Southport, Hesketh Park, 40. *Carbonaceous matter,* Newcastle, City Road, 9,736; Rothamsted, 630. *Insoluble ash,* Newcastle, City Road, 16,431; Kingston-on-Thames, 897. *Volatile salts,* Burnley, 7,513; London, Wandsworth Common, 752. *Soluble ash,* Burnley, 9,438; Rothamsted, 1,005. *Total deposit,* Burnley, 34,880; Southport, Woodvale Moss, 4,101. *Rainfall,* Burnley, 1,258 mm.; Kingston-on-Thames, 384 mm. The relation of the different components to the total pollution is given for London, Newcastle, Malvern, and Leeds for summer and winter; it shows a wide variation; *e.g.* at Newcastle, sooty matter formed 20·6 to 43·6 per cent. of the total, and at Malvern 3·3 to 8·6 per cent. The increasing use of gas accounts for some, at least, of the reduction in sulphates deposited in recent years.

SECTION II. AUTOMATIC FILTER.—The curves for the hourly variation of suspended smoky matter bring out the maximum and minimum times of pollution. The curves for South Kensington and Kew are lower than for Westminster, and maxima occur at different times. The effect of the coal stoppage in 1926 is shown from the continuous records of Stoke-on-Trent, and the reduction in the average shade numbers for the weeks compared with the corresponding weeks in 1925 is very marked.

SECTION III. JET DUST COUNTER.—Observations made with the Owens jet dust counter (ANALYST, 1926, **51**, 86; 1927, **52**, 155) are given from America, Melbourne, and Stockholm, and details of the method as used in America for sulphur determinations are included. The apparatus consists of two 20-litre bottles, one of which is connected with a manometer and hand pump; two smaller bottles (about 400 c.c.) are used as comparison bottles. The comparison bottles are filled with an equal quantity of solution made from distilled water, soluble starch, iodine and potassium iodide. The contents of one are emptied into one of the two 20-litre bottles and shaken. The other is similarly treated, but the pressure in the bottle is reduced to about one-half normal atmospheric pressure, the walls wetted with solution, and air drawn in. The solutions are emptied back into the comparison bottles, and, if there is a measurable quantity of sulphur in the air, the liquid is partially bleached. The colour is restored by titration with a weak

---

* Published August, 1928. Pp. 54. Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 6s. 6d. net.

solution of iodine, each c.c. of iodine solution added representing 0·05 part o sulphur in a million. Sulphur appeared to increase with increase in the dust particles.

The figures for the dust counts and sulphur determinations, made at the American University, Washington, in January, February and March, 1927, have been plotted, the sulphur contents as ordinates against the dust counts as abscissae. There was in this curve an obvious tendency for sulphur content to increase with dust content, but the method of sulphur determination was probably not sufficiently sensitive to give a reliable indication for small amounts, nor could a definite relation be established from plotting the two. The sulphur content ranged from 0 to 1·6 parts per million; the absence of measurable sulphur was usually obtained with dust counts of a few hundred particles per c.c., the 1·6 was obtained with a count of 3072. All that can be said from the available figures is that there is a tendency for the sulphur to increase as the dust particles increase, and both are doubtless caused by the drift of smoke from the city.

In Melbourne comparisons have been made between the results obtained with the Owens instrument and the Aitken counter.

It is now realised that the two methods count totally different particles, and, further, that to a great extent the particles dealt with by one method are excluded by the other. The Aitken method aims at counting anything which acts as a nucleus of condensation, whilst the Owens instrument aims at counting dust particles, and merely assumes that there will be always sufficient nuclei of condensation to provide liquid water to act as an adhesive.

Observations made by Ångström with the Owens dust counter in the neighbourhood of Stockholm show that, although the air is very pure, yet a considerable part of the dust present must be attributed to the effects of combustion.

Ångström suggests that, since the results obtained by the Owens method are to a certain degree dependent upon the magnification used in counting the particles, it would be advisable that in international work the number of particles counted by this method should be referred to a certain standard magnification, and he suggests 1000 diameters as convenient and practical. He states that no simple relation seems to exist between the dustiness expressed by the number of particles on the one hand and the meteorological elements at the moment when the sample was taken on the other, owing, no doubt, to the great number of factors influencing the amount of dust. Rain is stated to have the effect of clearing the air from dust; on the other hand, winds blowing over dry ground produce a dustiness which lasts for a long time after the storm has ceased.

Examination of Haze.—A method for examining haze, devised by Owens, consists in turning the open mouth of a shallow tin (about 4″ × 4″) to the wind, and allowing a jet of air to impinge on a slide held behind a circular hole cut in the bottom of the tin. The particles of a sea coast haze, trapped thus, consisted almost entirely of crystalline salts.

SECTION IV. OBSTRUCTION OF ULTRA-VIOLET RADIATION BY SMOKE.—Ultra-violet readings, plotted against smoke pollution shade numbers, show that there is a very evident relation. With a shade number a little over 6 the ultra-violet radiation is cut completely off, and as pollution approaches zero the curve tends towards the vertical. It would seem that the air must be sufficiently free from smoke to give about shade No. 1 on the automatic filter before any appreciable amount of ultra-violet radiation is allowed to reach the ground. This may be a guide in fixing clean air standards, but further experiments are needed to check these results.

D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Tests for the Soundness of Meat. L. M. Horowitz-Wlassowa. (*Z. Nahr. Genussm.*, 1928, **55**, 239–246.)—The alkalinity or acidity of aqueous meat extract, the P_H value, the refractive index, the intensity of the biuret reaction, the total nitrogen, the nitrogen precipitated by tannin or phosphotungstic acid, the oxidisability, and the iodine-fixing power are valueless as indications of the degree of freshness of meat. Eber's test for free ammonia often gives negative results with meat weeks old and even showing incipient putrefaction, and the blueing of red litmus by the vapour emitted when the meat is boiled with sodium hydroxide or magnesium oxide is of no practical value, as it indicates not only the ready-formed saline ammonia, but also the ammonia liberated during the heating. If, however, the comminuted meat (1 grm.) is extracted with ammonia-free water, the extract yields no ammonia from the amino-acids when heated for five minutes at 50° C. with magnesium oxide, although any ammonium salts present are decomposed under this treatment. Fresh meat, containing at most only very small proportions of ammonium salts, causes no blueing of red litmus paper when tested in this way, and a positive reaction shows the meat to be unwholesome. This test is much more sensitive than Eber's test and detects about 0·02 per cent. of saline ammonia. Valuable information is derivable also from titration of the free amino-acids by Sörensen's method. T. H. P.

Analysis of Vanillin and Vanillin Sugar. J. Pritzker and R. Jungkunz. (*Chem. Zeit.*, 1928, **52**, 537.)—Vanillin may be detected by means of Kreis and Studinger's modification (*Mitt. Geb. Lebensmittelunters. u. Hyg.*, 1928, **19**, 59) of Nickel's reagent ; 4·4 grms. of neutral potassium nitrite or 3·6 grms. of sodium nitrite are dissolved in 100 c.c. of saturated (about 7 per cent.) mercuric chloride solution, and the liquid mixed with 1 c.c. of 10 per cent. sodium carbonate solution. After the lapse of 15 minutes the precipitated brown basic mercuric carbonate is filtered off. The reagent should give a persistent wine-red coloration when heated for 15 minutes on a water-bath with an equal volume of 0·002 per cent. vanillin solution ; if vanillin sugar is to be tested, the aromatic ingredients must be first isolated by means of ether.

Determination of vanillin may be : (1) *Gravimetric* :—0·15 grm. of the vanillin is dissolved on a water-bath in 50 c.c. of water at 60° C., and, while hot, treated with 15 c.c. of an aqueous solution of 0·3 grm. of *m*-nitrobenzhydrazide. The solution is kept for 30 minutes at 60° C. on a water-bath, with frequent stirring, and, after 24 hours at room temperature, is filtered through a dry Gooch crucible, the precipitate being thoroughly washed with cold water, dried in an oven for

3 hours, and weighed. Multiplication of the weight by 0·4829 gives the vanillin. Since sugar gives no precipitate with *m*-nitrobenzhydrazide, the same method is applicable to vanillin sugar, 5–10 grms. of which should be dissolved in 50 c.c. of water. (2) *Volumetric* :—25 c.c. of 1 per cent. aqueous vanillin solution are titrated, in presence of 4 drops of 2 per cent. alcoholic thymolphthalein solution, to a distinct and persistent blue colour with 0·1 *N* sodium hydroxide solution ; 1 c.c. of the alkali corresponds with 0·0152 grm. of vanillin. With vanillin sugar, 15·2 grms. or the contents of an original package are dissolved in about 30 c.c. of water at 50–60° C. and titrated as above. The two methods yield closely concordant results. T. H. P.

Detection of Isopropyl Alcohol in Brandy by means of Piperonal. G. Reif. (*Z. Nahr. Genussm.*, 1928, **55**, 204–214.)—The fact that isopropyl alcohol may be manufactured by a simple process—either from acetylene, via acetaldehyde, acetic acid, and acetone, or from the propylene of petroleum, by way of isopropylsulphonic acid—renders necessary simple methods of testing for the presence of this alcohol in foodstuffs, etc. The means of detection now suggested is based on the formation of coloured compounds when the higher alcohols are treated with aromatic hydroxy-aldehydes together with a dehydrating agent. The best results are obtained with piperonal and, in testing brandy, if the distillate from this is diluted to contain 30 per cent. of alcohol by volume, the alcohols of the fusel oil present exert no disturbing influence on the reaction. Since, however, fermentation amyl alcohol is removable by charcoal, the following procedure is recommended :—The alcohol is distilled, on a water-bath, from 10 c.c. of the brandy into a small measuring cylinder standing in ice-water, and of the distillate, diluted with twice its volume of water, 0·3 c.c. is treated in a test-tube with 2 c.c. of water and 0·04 grm. of medicinal charcoal (Carbo medicinalis) and filtered through a dry paper of about 4·5 cm. diameter into a 100 c.c. boiling flask. The filtrate is treated with 5 c.c. of 5 per cent. alcoholic piperonal solution and slowly, with avoidance of boiling, with 20 c.c. of concentrated sulphuric acid (sp. gr. 1·84). After thorough shaking, 4–5 c.c. of the liquid are heated in a 50 c.c. beaker of 3–4 cm. diameter for 4–5 minutes on a boiling water-bath. In absence of isopropyl alcohol, a greenish-brown or brown coloration appears, presence of the alcohol being shown by a brownish-red or red colour. If the mixture in the beaker is treated, immediately after being heated on the water-bath, with 30 c.c. of a 30 per cent. solution of pure acetic acid, at most a transitory faint pink coloration is formed in absence of isopropyl alcohol, whilst in presence of the latter, a persistent pink or red colour appears. T. H. P.

Silver Benzoate Test for Olive Oil. (*Oil and Fat Ind.*, 1928, **5**, 206.)—The Olive Oil Committee of the American Oil Chemists' Society have carried out comparative tests for the detection in olive oil of olive oil extracted by carbon disulphide by the silver coin test, the acetic anhydride test, and the silver benzoate test. The committee recommends the last. Silver nitrate and sodium benzoate are mixed in hot aqueous solution, the mixture cooled, and the precipitated silver benzoate collected, washed and dried. Twenty mgrms. of the dry benzoate are added to 5 c.c. of the oil, and the mixture heated to 150° C. in an oil bath. Even with an oil containing only 1 per cent. of extracted oil a definite brown coloration is obtained, which may easily be distinguished from that produced by pure olive oil.

R. F. I.

The Composition and Constants of Avocado Oil. G. S. Jamieson, W. F. Baughman and R. M. Hann. (*Oil and Fat Ind.*, 1928, **5**, 202.)—Californian avocado fruit pulp contains over 70 per cent. of fat on a moisture-free basis. Even when purified, the fat is still dark green in colour and can therefore probably only be used for soap-making. A sample contained the glycerides of the following fatty acids :—Oleic, 77·3 ; linolic, 10·8 ; myristic, trace ; palmitic, 6·9 ; stearic, 0·6 ; arachidic, trace ; and unsaponifiable matter, 1·6 per cent. Its constants were : Sp. gr. at 25°/25° C., 0·9132 ; n_D^{20}, 1·4700 ; acid value, 2·8 ; saponification value, 192·6 ; iodine value (Hanus), 94·4 ; acetyl value, 9·2 ; Reichert–Meissl value, 1·7; Polenske value, 0·2; saturated acids, 7·2 per cent.; and unsaturated acids, 84·3 per cent.

R. F. I.

Tests for the Incipient Rancidity of Fats. W. L. Davies. (*J. Soc. Chem. Ind.*, 1928, **47**, 185–187T.)—The more important tests suggested for tracing the course of the auto-catalytic oxidation of fats are discussed. An indication, not of the degree of rancidity, but of the amount of three-membered carbon chain compounds capable of coupling together two molecules of phloroglucinol to form a flavonium salt, is furnished by the Kreis test, in which the fat is mixed with concentrated hydrochloric acid and an ethereal solution of phloroglucinol, an oxidised or rancid fat imparting a red colour of varying intensity to the aqueous phase (*cf.* Holm and Greenbank, ANALYST, 1923, **48**, 608).

The keeping qualities of a fat may be forecast from the results of the following test : 1 c.c. (or grm.) of the oil or fat is well shaken with 5 c.c. of separated milk diluted with an equal quantity of water, and 1 c.c. of a 0·25 per cent. solution of methylene blue added. The more bacteria of natural occurrence present in the milk the better, since the amount of reductase which causes the blue colour to disappear is roughly proportional to the number of bacteria present, and the "dirtier" the sample of separated milk, the quicker will be the reduction and the more rapid the test. The shaking of the fat with the milk partly emulsifies it, and the oxidising compounds are in contact with the aqueous phase. The tubes are incubated at 37–40° C. until the blue colour disappears, and when all the tubes are colourless the same conditions of the fat as to initial oxidation prevail, there being no peroxide or dissolved oxygen present. The tubes are then shaken vigorously for 15 seconds and left for 2 minutes, during which time the use which the fats can make of the same amounts of dissolved oxygen may be compared by the different degrees to which the blue colour is restored. Thus, the relative depths of blue are quantitative indications of the oxidation capacities of the fats. Application of this procedure to a large number of oils of different origins and known histories showed that the depths of colour developed were approximately in direct proportion to the acidities, and the results agreed uniformly with the observed keeping qualities.

The test was applied also to the detection of metallic contamination of butter fat, samples of butter being made which contained, as lactates, 2 and 10 parts of copper per million, or 10 and 25 parts of iron per million, together with salt ; a control sample with salt alone was also prepared. Five such series of five samples were prepared from creams ripened to various acidities and variously treated. With the newly-made butters, a few hours after the introduction of the catalyst the colour was restored to the butter-methylene blue mixtures in exact proportion to the amount of the metal present. Copper proved to be twelve times as active a catalyst to fat-oxidation as iron, this result being borne out by those of successive tests made to trace the development of rancidity in the butters. T. H. P.

New Fatty Acid from a Fish Oil. H. Marcelet. (*Compt. rend.*, 1928, **187**, 145–146.)—A fatty acid (dorosomic acid), m.pt. 55°, was isolated by the lead salt and Heintz methods from the oil of *Dorosoma nasus*, Bloch. It is soluble in hot alcohol, crystallising, on cooling, in small needles ; soluble in chloroform, ether and benzene. Two samples contained 74·53, 75·25 of carbon and 12·66 and 12·76 of hydrogen, thus corresponding to the acid $C_{17}H_{34}O_2$ of molecular weight 270. The acid had a neutralisation value of 207·39 (theory 207·7) and a content of barium from the Heintz fractions of 20·14 (theory 20·29), the lead salt containing 27·14 per cent. of lead (theory 27·78). This acid, not previously isolated from an animal oil, bears a close resemblance to daturic acid from *Datura stramonium*, with which it may possibly prove to be identical. D. G. H.

Infusion of Senega. J. F. Liverseege. (*Pharm. J.*, 1928, **121**, 90–91.)—Infusion of senega, as dispensed, and concentrated infusions, were found to show great variation in composition, the total solids in dispensed infusions varying from 0·4 to 1·36 per cent., and alkalinity (c.c. normal per bottle) from 38 to 87. Senega roots and infusions showed much less variation. It is considered desirable that the next Pharmacopoeia should give a formula for one-eighth concentrated infusion and call it "Infusum Senegae," and that the name of the present preparation should be altered to "Infusum Senegae Recens" (see also p. 491). D. G. H.

Fluid Extract of Senega Root. P. Fischer and P. Horkheimer. (*Süddeutsche. Apoth. Ztg.*, **68**, 188 ; *Pharm. J.*, 1928, **121**, 37.)—Saponins are determined in fluid extract of senega root by determining the haemolytic index by removing the alcohol from 1 c.c. of extract at 70° C., drying the residue, and preparing a 0·5 per cent. solution (a 10 per cent. solution was necessary with one inferior preparation). Physiological sodium chloride solution (with $M/15$ phosphate buffer solution of P_H 7·3) was used as solvent, and 1 c.c. of a 2 per cent. suspension of defibrinated human blood, prepared with the phosphate buffer mixture, was used in each test-tube, and made up to 2 c.c. with the sodium chloride buffer mixture, and 0·5 per cent. senega extract solution was added in quantities from

0·1 to 1 c.c. (0·1, 0·15, 0·2 . . .). The tubes were lightly shaken, left for 10 minutes, shaken and examined after 15 hours. The tube in which total haemolysis first takes place is taken for calculation of the haemolytic index, and the next one, with slightly lower saponin content, must show a distinct turbidity on shaking.

Senega fluid extracts of various sources.	1.	2.	3.	4.	5.	6.	7.
Haemolytic index	57	1,100	1,100	670	1,100	620	570
Dry residue, per cent.	8·8	26·7	28·6	27·6	24·5	21·3	27·1
Ash, per cent.	0·58	1·4	0·92	0·95	1·3	0·71	1·0

Under certain conditions the height of froth formed by saponin-containing substances and the haemolytic index are proportional, and use may be made of this as a simple preliminary test. D. G. H.

Detection of Cocaine by Guerbet's Reaction. Guigues. (*Ann. Chim. Analyt.*, 1928, **10**, 201–202.)—In using Guerbet's reaction (ANALYST, 1920, **45**, 334) for detecting cocaine it is necessary that the solution of stannous chloride should be slightly acid. D. G. H.

Identity of Yohimbine and Quebrachine. Raymond-Hamet. (*Compt. rend.*, 1928, **187**, 142–145.)—Yohimbine was prepared from Gustrow's yohimbine hydrochloride and identified with authenticated yohimbine from the bark of *Pausinystalia johimbe,* and quebrachine from the bark of *Aspidosperma quebracho blanco.* Yohimbine contained 71·28 and quebrachine 71·02 of carbon, and 7·54 and 7·46, respectively, of hydrogen. The m.pts. were the same (259°–260° C.), rotatory power in pyridine +135·9° and +136·7° ; m.pt. of ethyl yohimbate and quebrachate 189°–190° C., and their rotatory powers in absolute alcohol +54·3 and +53·5. The propyl compounds also had the same m.pts. (136°–137° C.), with rotatory powers, +48·1 and +47·8. The lethal doses for guinea pigs were the same, and both substances paralysed the sympathetic nervous system. Yohimbine and quebrachine are concluded to be identical. D. G. H.

Apiol. J. F. Walmsley. (*Pharm. J.*, 1928, **121**, 89–90.)—The only substance correctly designated apiol is the crystalline constituent of parsley oil, and the only body worthy of the name "liquid apiol" appears to be essential oil of parsley, and that only if derived from an apiol-bearing variety of parsley, since the non-fatty matter of the ethereal extract of English and French-grown parsley fruits appears to be chiefly myristicin, not apiol. *Carum petroselinum,* B. and H., *petroselinum sativum,* Hoffman, and *Apium petroselinum* L., yield apiol. The liquid green apiol of commerce does not agree with the B.P.C. description, and an ethereal extract of parsley seeds is a fatty oil containing a small proportion of non-fatty matter and cannot pass the specific gravity and solubility tests of the B.P.C. D. G. H.

Test for the Activity of Medicinal and other Charcoals. H. Brindle. (*Pharm. J.*, 1928, **121**, 84.)—The charcoals, after drying at 110°–120° C., are exposed in thin layers to air saturated with water, alcohol, or turpentine, and the percentages by weight of vapour absorbed ascertained. With eight samples of different kinds of charcoal the percentage of alcohol vapour absorbed varied from **9·43** (levigated charcoal, pharmaceutical quality) to **84·49** per cent. (experimental sample). Active charcoal will absorb **50** to **100** per cent., or even more, of moisture, and similar absorption figures are given with water, alcohol and turpentine.

D. G. H.

Comparison of the Absorptive Power of Medicinal Charcoals. H. Brindle. (*Pharm. J.*, 1928, **121**, 84–85.)—Absorption powers of charcoals were compared by means of the moisture absorption test (see above), a slight modification of Miller's benzoic acid absorption test, and the mercuric chloride test of the German Pharmacopoeia. All samples of ordinary medicinal charcoal were comparatively inactive, and, since their medicinal use depends on their activity, their preparation by some modern process, such as the steam process, is recommended, and an activity test should be included in the new Pharmacopoeia.

D. G. H.

Enamel containing Antimony. F. M. Litterscheid. (*Z. Nahr. Genussm.*, 1928, **55**, 296–297.)—Culinary vessels lined with enamel, in the preparation of which an antimony-containing substitute is used in place of tin oxide, mostly yield considerable proportions of antimony to 4 per cent. acetic or tartaric acid solution, so that their use may be attended with the introduction into food of organic antimony compounds with emetic properties. T. H. P.

Biochemical

Colorimetric Method for the Determination of Free Tryptophane in Blood. C. A. Cary. (*J. Biol. Chem.*, 1928, **78**, 377–398.)—A more satisfactory method than those previously used is described for the determination of protein-free tryptophane in blood and blood plasma. The procedure depends upon the familiar Hopkins–Cole reaction with glyoxylic acid and the oxidation of the tryptophane-glyoxylic acid condensation product by means of mercuric sulphate. The method, like that of Cary and Meigs (*J. Agric. Research*, 1924, **29**, 603) with *p*-dimethylaminobenzaldehyde, is not specific for tryptophane, but gives colours of varying character with other indole derivatives. The method is applied to mercury precipitates from deproteinised blood extracts. Correction must be made for the loss of the tryptophane in this precipitation, and then good agreement is obtained with standards which contain 0·265 mgrm. or more of tryptophane, and with blood or blood plasma samples of 25 c.c. or more. Tryptophane added to the blood is recovered quantitatively. When determined colorimetrically the colours of the blood and standard match readily, but when analysed spectrophotometrically this agreement is found not to be perfect. Apparently 75 to 85 per cent. of the material in the blood that is finally determined colorimetrically as tryptophane, according to the method described, is actually such, either being free or derived from simple peptides in the blood ; but 15 to 25 per cent. of it is not.

This material, however, may be partly derived from tryptophane originally present in the blood, and therefore the colorimetric method, as described, gives a fairly close approximation to the actual tryptophane present. P. H. P.

Determination of the Guanidine Bases in Urine. C. J. Weber. (*J. Biol. Chem.*, 1928, **78**, 465–473.)—A colorimetric method for the determination of guanidine in urine is described which shows a high percentage of recovery when guanidine is added to normal urine, and should prove useful in a study of the fate of these compounds when they are introduced into the body. Normal urine gives a colour with this reagent, but the substance responsible for the colour production is not yet known; owing to the number of interfering substances present, no direct determination of guanidine in the urine is possible. The paper deals with the determination of the three simple guanidine bases: guanidine, methylguanidine and *as*-dimethylguanidine. Guanidine gives an orange-red colour, but the other two bases give more of a red and less orange. Methylguanidine is almost equivalent in the amount of colour produced to guanidine, whilst 1 mgrm. of dimethylguanidine is equivalent to 0·58 mgrm. of guanidine. For the colour reagent (an alkaline nitroprusside-ferricyanide solution) equal volumes of 10 per cent. solutions of sodium nitroprusside, potassium ferricyanide and sodium hydroxide are mixed, and the mixture is diluted with 3 vols. of water. After 30 minutes the reagent is of a pale orange-yellow colour and is ready for use. It will keep for several hours, but must be freshly made when markedly turbid. To every 5 c.c. of the solution to be tested, 1 c.c. is added. For the guanidine standard, 0·1524 grm. of guanidine carbonate is dissolved in 100 c.c. of 0·1 *N* hydrochloric acid; this contains 1 mgrm. of guanidine per c.c. Five c.c. of this, diluted to 250 c.c., contain 0·02 mgrm. of guanidine per c.c.; the solutions are preserved with chloroform. For the method, 10 c.c. of 40 per cent. lead acetate and 5 c.c. of 10 per cent. sodium hydroxide are added to 25 c.c. of urine in a 50 c.c. centrifuge tube, shaken, and centrifuged after 30 minutes. Twenty c.c. of the clear supernatant liquid are pipetted into another centrifuge tube, treated with 10 c.c. of saturated disodium phosphate, and mixed. The lead phosphate precipitate is removed by centrifuging and the liquid decanted. Twenty-five c.c. are extracted by the addition of 1 c.c. of 10 per cent. sodium hydroxide and 2 grms. of acid-washed norit, the norit being brought into suspension by shaking. The mixture is filtered through an asbestos mat on a Gooch crucible. The charcoal is washed with two 10 c.c. portions of water made alkaline with 2 or 3 drops of 10 per cent. sodium hydroxide, then again with 10 c.c. portions of alcohol which contains 6 c.c. of *N* hydrochloric acid per 100 c.c., and the filtrate is caught in a test-tube. Forty c.c. of alcohol are used, and this filtrate, after the addition of 5 c.c. of 5 *N* hydrochloric acid, is evaporated to dryness on a water-bath. The residue is dissolved in 20 c.c. of water, and 5 to 10 c.c. are taken for the colorimetric determination. The standards are 0·07, 0·1, 0·15 and 0·2 mgrm. of guanidine per 10 c.c., and 2 c.c. of the reagent added. The unknowns are made to the same volume, and 2 c.c. of reagent added. The readings are made after 5 minutes, and must be completed 9 minutes after the addition of the reagent. If one-half of the residue is used for analysis, the guanidine content of urine is : $\frac{20}{\text{Reading of unknown}} \times$ mgrm. of guanidine in standard × 19·2 mgrm. guanidine per 100 c.c. urine. A determination is completed in about 2 hours. P. H. P.

The Rennin Coagulation of Milk. Effect of Hirudin, of Heparin, of Cephalin and of Fat Removal. J. B. Stone and C. L. Alsberg. (*J. Biol. Chem.*, 1928, **78**, 557–572.)—The rennin coagulation of milk has been described as resembling in many ways the fibrin ferment coagulation of blood, and it was thought that some of the agents that inhibit or favour fibrin ferment action may have analogous effects upon rennin action. Hirudin and heparin, as blood coagulation-inhibiting agents, and cephalin, as a blood coagulation-favouring agent, were used for the investigation. To determine the effect of cephalin upon rennin coagulation of milk, it was found necessary to remove lipoid, and, therefore, to study the effect of fat solvents upon rennin and upon milk, and also the effect of skimming upon milk coagulation. Neither hirudin nor cephalin exerts any influence on the rate of coagulation of milk by rennin. Heparin may, or may not, delay the coagulation. Some preparations delayed it notably, others delayed it but slightly, or not at all ; yet all had about the same effect upon blood coagulation. Therefore, heparin preparations which delay rennin coagulation must be regarded as mixtures which contain both blood coagulation-inhibiting and milk coagulation-inhibiting material. There is no evidence that the two effects are connected in any way. Heparin preparations which delay rennin coagulation of milk act upon the rennin rather than upon the milk. When a rennin solution has the fat and lipoid extracted with pure ether, and is left saturated with ether for a considerable time, its coagulating power is not affected. Pure ether, ethyl alcohol and chloroform inhibit the rennin coagulation of milk when present in sufficient quantity. Benzene delays coagulation slightly, petroleum spirit still less. Probably the effect is not due only to lowering of surface tension, for saponin is without effect. A neutralised soap solution greatly delays coagulation, but the effect is probably due mainly to the removal of calcium ions, since the addition of small amounts of calcium chloride prevents the effect. Milk skimmed by a separator coagulates more slowly than milk skimmed by gravity. P. H. P.

The Absorption Spectrum of Vitamin *A*. R. A. Morton and I. M. Heilbron. (*Nature*, 1928, **122**, 10.)—Both provitamin *D* and the antirachitic vitamin itself exhibit photochemical properties. The action of light on vitamin *A* was previously thought to be an indirect oxidation process, but it is now definitely proved to be a purely photochemical mechanism. The authors have shown, by a spectrographic study of cholesterol from cod-liver oil that provitamin *D* exhibits selective absorption in the ultra-violet. Three absorption bands at $293{\cdot}5\mu\mu$, $281{\cdot}5\mu\mu$ and $270\mu\mu$ were observed, and shown to be criteria of provitamin *D*. This discovery paved the way to the recognition of ergosterol as the photochemical precursor of vitamin *D*. To test the hypothesis that vitamin *A* should exhibit selective absorption in the visible or near ultra-violet, rich sources of vitamin *A* were necessary. Cod-liver oil is the best known source of this vitamin, and several other workers have found the oil to show the absorption band at $328\mu\mu$. Therefore, it seemed reasonable to think that this band is connected with vitamin *A*, since no other constituent of cod-liver oil is known to show a band in this region of the spectrum. A large and varied assortment of fish liver oils and vitamin *A* concentrates has now been collected, and a detailed spectrographic examination made of the samples. The chief result is the record of a prominent absorption band at $328{\cdot}5\mu\mu$, the intensity of which runs closely parallel with the vitamin *A* potencies of the various oils, as measured by the antimony trichloride colour test. Irradiation results in the disappearance of the chromogenic substance. Biological experiments have proved that aeration or oxidation also causes the destruction of the vitamin, and the spectrographic tests show the same result. Probably the first decomposition products of vitamin *A* include a substance which possesses an absorption band in the region 275–$285\mu\mu$. " Non-saponifiable " extracts show the $328\mu\mu$ band. The adoption of the $328\mu\mu$ band as a criterion of vitamin *A* will, it is hoped, assist in the elucidation of the chemical nature of the substance. The test is less empirical, but probably more trustworthy, although sometimes less delicate, than the antimony trichloride reaction. P. H. P.

Relative Stability of Vitamin *A* from Plant Sources. H. C. Sherman, E. J. Quinn, P. L. Day, and E. H. Miller. (*J. Biol. Chem.*, 1928, 78, 293–298.)—An investigation has been made which included, first, experiments to determine the effects of heat, in the presence or absence of oxygen and at different hydrogen ion activities, upon the vitamin *A* which occurs in a primary or plant source, and then parallel experiments to compare the stability of this vitamin as obtained from a plant and an animal source. The relative amounts of vitamin *A* were measured by feeding experiments on rats. Vitamin *A* from plant sources is shown to be relatively stable. When tomato juice was heated at 97° C. ±2° C. for 4 hours in an atmosphere of nitrogen, the destruction of vitamin *A* was found to be about 17 per cent. ; when air was bubbled through the juice continuously during the heating process, the destruction was not measurably increased. The stability of vitamin *A* in tomato juice, when heated at 98° C. ±2° C. for 4 hours in an atmosphere of nitrogen, was found to be the same at P_H 9·2 as at P_H 4·2, the normal acidity of the juice. When heated under anaerobic conditions for 4 hours at 97° C. ±2° C., the vitamin *A* contained in an olive oil extract of dry spinach was found to be somewhat more stable than was the vitamin *A* in an olive oil solution of butter fat heated under the same conditions. The destruction of the vitamin *A* from spinach was about 20 per cent., whilst the destruction of that from butter was about 33 per cent. It would be premature to discuss the question whether the destruction of vitamin *A* here observed may have been due to an oxidation reaction, even though dissolved and atmospheric oxygen had been excluded.

P. H. P.

The Tripartite Nature of Vitamin *B*. R. R. Williams and R. E. Waterman. (*J. Biol. Chem.*, 1928, **78**, 311–322.)—By a series of rigid experimental comparisons of the dietary requirements of growing rats and adult pigeons the authors have concluded that vitamin *B* consists of three factors. The first is the relatively thermolabile antineuritic vitamin, the second is the relatively stable factor which Goldberger and others have associated with the prevention of pellagra, and the third is highly thermolabile, and so far has been associated only with the maintenance of weight and general condition of adult pigeons. Further evidence is given as to the second factor of vitamin *B*, verifying the conclusion that it is potent for rats, but not noticeably so for pigeons, and it is shown that there is the third factor of vitamin *B*, potent for pigeons but apparently not for rats. As a source of the antineuritic factor of vitamin *B* a special form of fullers' earth preparation of brewers' yeast, which was developed in the course of attempts to isolate the antineuritic vitamin, was used. It is produced when a limited amount of fullers' earth is brought into contact with yeast extract with the intervention of a collodion membrane. The details of the method for its production are given, together with a diagram of the dialysis and adsorption apparatus used. Polished rice, or, in some cases, the synthetic diet, was given to the pigeons, and autoclaved brewers' yeast was the source of the second factor of vitamin *B*. Pigeons which had been brought to a sub-normal level on the synthetic diet, supplemented by special fullers' earth, or on polished rice, soon attained a normal weight level, and generally improved when given whole wheat, or when 1 grm. of air-dried brewers' yeast was added every other day to the basal diet. Since this result was not obtained with autoclaved yeast or special fullers' earth preparation of yeast, or both, as supplements, the improvement in weight and condition of the birds must have been due to a thermolabile factor originally present in the yeast, which is different from the antineuritic factor. It was shown that this third factor was not vitamin *A*, *D* or *E*. P. H. P.

The Plural Nature of Vitamin *B*. A. G. Hogan and J. E. Hunter. (*J. Biol. Chem.*, 1928, **78**, 433–444.)—Previous workers have shown results which suggest the possibility that vitamin *B* is a mixture of two components, and that one is destroyed by irradiation, and the other by high temperatures. It was decided to examine a single preparation, in itself a complete source of vitamin *B*, but which with suitable manipulation would show on the one hand only antineuritic activity, on the other only growth-promoting activity, to study each of these modified preparations, and also to determine whether there is any supplementary relation between them. Harris dried yeast and a vitamin *B* concentrate prepared from fresh brewers' yeast were the sources of vitamin *B*, and as experimental animals, rats, chicks and pigeons were used. Under the experimental conditions observed, vitamin *B* carriers become inadequate after exposure to ultraviolet rays for a period of 10 hours. These irradiated materials retain antineuritic activity, but lose their so-called growth-promoting properties. Autoclaved yeast loses its antineuritic potency, but, as shown by other workers, retains growth-promoting activity. Irradiated and autoclaved vitamin *B* preparations are both inadequate when used as the sole source of the vitamin. There is a supplementary relation between them, however, and a mixture of the two is a potent source of vitamin *B*. Vitamin *B*, therefore, as the term has been used in the past, is a mixture of at least two distinct vitamins. The authors consider the designation "growth-promoting," as applied to a vitamin *B* constituent, to be unsuitable, for, in the same sense that it promotes a more normal nutritional condition, the antineuritic, antiophthalmic, antiscorbutic and antirachitic vitamins are also growth-promoting. The term "antidystrophic" is less objectionable and less misleading. It is suggested that the designation vitamin *B* should be reserved for the antineuritic factor, and that the so-called growth-promoting factor should be given an individual designation and be known as vitamin *F*.

P. H. P.

Malt Extracts and Oil Emulsions. I. Composition of Commercial Malt Extract and Cod-Liver Oil Emulsions. J. M. Jones and J. McLachlan. (*Pharm. J.*, 1928, **121**, 91.)—Of twelve samples of cod-liver oil and malt extract emulsions, the majority contained 2·5 to 19·81 per cent. of oil. Tables given include figures for the oil, total solids of the extract, diastatic activity of the malt (24 to 1060) and percentage by weight of alcohol. The flavourings were usually about 0·02 per cent.

D. G. H.

II. Vitamin *A* content of Commercial Malt Extract and Cod Liver Oil Emulsion. J. M. Jones and N. Evers. (*Pharm. J.*, 1928, **121**, 91.)—The vitamin *A* content of a number of commercial samples of malt extract and cod-liver oil emulsions was determined by the antimony trichloride test of Carr and Price, and the number of blue tintometer units converted into values approximately corresponding to the U.S.P. biological units, by the factor 85. Good Norwegian cod-liver oil of medicinal quality contains, on an average, 500 units of vitamin *A* per grm. The results varied from nil units per grm. of oil (2 samples), 160 (1 sample), 300 (1 sample), 460 (2 samples), to 840 (2 samples). A 23-year-old sample gave a colour test of 250 units.

D. G. H.

III. Testing of Malt Extract and Cod-Liver Oil Emulsions for Vitamin *A*. J. M. Jones and N. Evers. (*Pharm. J.*, 1928, **121**, 91–92.)—The use of calcium chloride for drying solutions of cod-liver oil to be tested for vitamin *A* should be avoided, since comparative tests indicated that the destruction of the vitamin was much greater in the presence of calcium chloride than in its absence. Chloroform solutions of cod-liver oil kept their activity longer than petroleum spirit solutions, and exposure to daylight appeared to accelerate the loss of activity.

D. G. H.

The Biological Assay of Cod-Liver Oil. G. Adams and E. V. McCollum. (*J. Biol. Chem.*, 1928, **78**, 495–524.)—A method for the biological assay of cod-liver oil is described, and results are given in detail. Rats were fed on a rickets-producing diet for a certain preliminary period until rickets should develop, as determined by histological examination of the bones of a control group. Cod-liver oil in minimal amounts was then added to the ration, and the rats were kept on this diet for a test period of a few days and then killed ; the bones were examined histologically by the " line test " to determine the degree of healing. A control group, however, was continued on the rickets-producing diet alone (*i.e* no cod-liver oil added) to the end of the test period, in order to indicate whether changes in the test group were really due to the influence of the cod-liver oil. The femurs of typical rats from each group were analysed for ash, calcium and phosphorus ; and serum from the pooled blood of each group was likewise analysed for calcium and phosphorus content. The data obtained do not bear out the anticipated possibility of the determination of the antirachitic potency of cod-liver oils by following changes in bone composition. Blood analyses, calculated to give the ion product values $[Ca^{++}]^3 \times [PO^{\equiv}_4]^2$, indicate whether test animals show active rickets or healing. Values less than 8×10^{-25} indicate active rickets, but values greater than 8×10^{-25} indicate healing or absence of rickets. Indications such as those given by results of blood analyses can be correlated with line test (*i.e.* histological) observations in almost all cases. The line test picture, as shown by the majority of a group of 10 or 15 animals, should be indicative of the potency of a given oil. Cod-liver oils do vary with respect to their content of antirachitic vitamin. The method used for the assay of cod-liver oil gives data which show only the relative potency of oils. Absolute comparison to the point of the establishment of so many arbitrary units of antirachitic factor per given weight of oil is not justified on the basis of data of the type obtained. A given procedure is no more accurate than the least accurate of the factors involved; biological behaviour is not assessable with mathematical accuracy, and, therefore, no biological assay with respect to the vitamin content of given substances will yield more than relative values. The dosages ordinarily indicated, and the time period usually involved in the utilisation of cod-liver oil for prevention or cure of human rickets, allow such a factor of safety that it is probable that any of the better grades of oil upon the market afford protection. P. H. P.

Organic Analysis.

Identification and Separation of Urotropine and Formaldehyde in Mixtures. M. V. Jonescu. (*Bull. Soc. Chim.*, 1928, **43–44**, 677–680.)—The difference in the rate of reaction with dimethylhydroresorcinol in the cold between urotropine and formaldehyde allows these compounds to be detected in the presence of each other. To the mixed solution a solution of dimethyldehydroresorcinol is added in excess, and, after 15 minutes, the mass of fine needle-shaped crystals of methylene-bis-dimethylhydroresorcinol formed from the formaldehyde is filtered off. The filtrate, thus freed from formaldehyde, is boiled, and the methylene-*bis*-dimethyldehydroresorcinol formed from the urotropine is decomposed and a white precipitate obtained. D. G. H.

Inorganic Analysis.

Detection of Arsenic in the Presence of Selenium. E. Guérin. (*Bull. Soc. Pharm. Bordeaux*, 1927, **65**, 152 ; *J. Pharm. Chim.*, 1928, **120**, (vii), 620–621.)—Arsenic may be detected in the presence of selenium by precipitating the selenium by Bougault's mercury reagent (mercurous nitrate, 10 grms., nitric acid (sp. gr. 1·9), 10 c.c., water 100 c.c.), and, after filtration, eliminating the bulk of the mercury by hydrochloric acid. Arsenic is precipitated from the filtrate by ferric hydroxide with just sufficient ammonia, the precipitate collected, washed, treated with hydrochloric acid, and the solution used for the determination of the arsenic by Bougault's reagent. D. G. H.

Determination of Cadmium and Zinc. G. Spacu and J. Dick. (*Z. anal. Chem.*, 1928, **73**, 279–283, 356–359.)—Cadmium and zinc can be determined gravimetrically as complex pyridine thiocyanates, $(M''Py_2)(SCN)_2$; the method is the same as that used for cobalt and nickel (ANALYST, 1927, **52**, 660). W. R. S.

Separation of Beryllium from Aluminium by Hydroxyquinoline. I. M. Kolthoff and E. B. Sandell. (*J. Amer. Chem. Soc.*, 1928, **50**, 1900–1904.)—The present method is stated to be more simple and rapid than that of Moser and Niessner (ANALYST, 1928, **53**, 401). It is based on the precipitation of aluminium by *o*-oxyquinoline in weakly acid acetate solution as $(C_9H_6ON)_3Al$ (ANALYST, 1927, **52**, 612). The reagent is a 5 per cent. solution of the finely-powdered base in 2 *N* acetic acid. The slightly acid solution, containing not more than 0·1 grm. of either oxide per 100 c.c., is treated at 50° C. with an excess of the reagent. Ammonium acetate solution (2 *N*) is added until a permanent precipitate is obtained, and is followed by another 20 to 25 c.c. of the same reagent to complete the precipitation. After settling, the precipitate is collected on a porous glass or porcelain crucible, washed with cold water, and dried at 120° to 140° C. (Al_2O_3 factor $=0·1110$). The filtrate is heated nearly to boiling, and ammonia in faint excess cautiously added. The yellow to brown precipitate is collected and well washed with a hot dilute solution of ammonium acetate containing a few drops of ammonia. The precipitate is dried over a low flame in a platinum crucible and ignited over a blast burner. The beryllium oxide must be weighed quickly, as it is slightly hygroscopic. The results are good, the alumina figues being slightly low, and the beryllia results correspondingly high. Ferric iron is precipitated like aluminium ; two separations of beryllia from ferric oxide gave satisfactory results. The iron precipitate is black. In the separation of much beryllium from little aluminium an excess of 50 per cent. of the reagent is recommended for reducing the solubility of the aluminium precipitate. In the opposite case an excess of 10 to 20 per cent. suffices ; it is also considered advisable to weigh small quantities of beryllium as the anhydrous sulphate, after evaporation of the oxide with a few drops of sulphuric acid and heating to constant weight at 350° to 400° C.

W. R. S.

Determination of Manganese. G. Spacu and J. Dick. (*Z. anal. Chem.*, 1928, **74**, 188–191.)—The cold (15° C.), neutral solution (50 to 100 c.c.) is treated with 1·5 grms. of solid ammonium thiocyanate, then 4 c.c. of pyridine, and the white crystalline precipitate of $(\mathrm{Mn}Py_4)(\mathrm{SCN})_2$ collected after 3 minutes on a porous crucible, and washed like the corresponding nickel compound (ANALYST, 1927, **52**, 660). It is weighed after being dried *in vacuo* to constant weight (Mn factor = 0·1127). W. R. S.

Colorimetric Determination of Titanium. F. G. Germuth. (*J. Amer. Chem. Soc.*, 1928, **50**, 1910.)—In the colorimetric process by hydrogen peroxide, phosphoric acid is known to produce a slight fading of the colour. It was found that the addition of uranium acetate (1 c.c. of 0·1 per cent. solution per 0·0001 grm. Ti) to the acid solution counteracts the influence of the phosphoric acid. This effect is stated to be independent of the amount of phosphoric acid or phosphate present. W. R. S.

Determination of Free Alkali in Hypochlorite Solutions. E. Rupp and F. Lewy. (*Z. anal. Chem.*, 1928, **73**, 283.)—The solution of hypochlorite (hypobromite) is stirred and treated with small portions of neutral hydrogen peroxide until effervescence ceases. The alkali hydroxide and carbonate are then titrated as usual against methyl orange. An undue excess of peroxide bleaches the indicator ; if so, the liquid is boiled for a few minutes, cooled, and treated with fresh indicator. W. R. S.

New Indicator for the Volumetric Determination of Phosphoric Acid. L. Duparc and E. Rogovine. (*Helv. Chim. Acta*, 1928, **11**, 598–599.)—Titration of phosphoric acid with uranyl acetate in presence of tincture of cochineal does not yield a sharp end-point, and is almost useless for urine, whilst the drop test for the end of the reaction by means of potassium ferrocyanide is very delicate and unfitted for the use of beginners. Satisfactory results are obtainable by taking advantage of the fact that sodium salicylate and uranyl acetate form an intensely orange double salicylate. Use is made of a solution containing 13–15 grms. of uranyl acetate per litre, which may be standardised against a solution prepared by dissolving 5·46 grms. of tricalcium phosphate in nitric acid and diluting to 1 litre. To 20 c.c. of this solution, and to 20 c.c. of that to be tested, are added 50 c.c. of water and 10 c.c. of 10 per cent. sodium salicylate solution. Each of the liquids is heated to boiling and titrated with the uranium solution to an orange-yellow solution. The precipitate formed settles quickly, and the colours of the two liquids are then compared either in presence of the precipitate or after its removal by deposition or by centrifuging. In examining urine 10 c.c. of the sample are diluted with 60 c.c. of water, the amount of the tricalcium solution taken being brought to the same volume ; at this dilution the colour of the urine does not disturb the colour change of the reaction. T. H. P.

Physical Methods, Apparatus, etc.

Apparatus for Determining Molecular Weights by the Boiling Point Method. H. Rupe and N. Wassilieff. (*Helv. Chim. Acta,* 1928, **11,** 713–716.)—In the apparatus described, the boiling vessel consists of a test-tube of good quality, about 190 mm. long and 31–32 mm. wide, and having sealed to it, somewhat below the mouth, an inner, open-ended jacket, A, 70 mm. in length, the space between the two tubes being 1·5–2 mm. Just below the top of the inner jacket is a side-tube B, connected with a small condenser, C, by a ground joint. The most important part of the apparatus is a tube D (Fig. 2), 130 mm. high, funnel-shaped at the base, standing on three feet, and branched at the top to form three tubes with somewhat narrow orifices. The short thermometer, E, such as is used with the Landsberger apparatus, reads to 0·05° C., and is held by a cork so that its bulb is between the three branch tubes. When the liquid boils, solvent (or solution) and vapour impinge on the thermometer bulb, and the vapour partially condenses. For acetone, the dimensions of the boiling tube are as shown in Fig. 2 ; for benzene or water, the width is 5·1 mm. below and 3·9 mm. above; and for chloroform, 3·9 mm. below and 2 mm. above. Retardation of the boiling is prevented by a few small fragments of porous tile, but with water a few scraps of platinum are required. Heating is effected by a Bunsen burner with the tube removed, the flame, protected by a cylinder of asbestos paper, being about 10 cm. below the apparatus. With acetone or chloroform, a determination may frequently be completed in 20 minutes, but with water

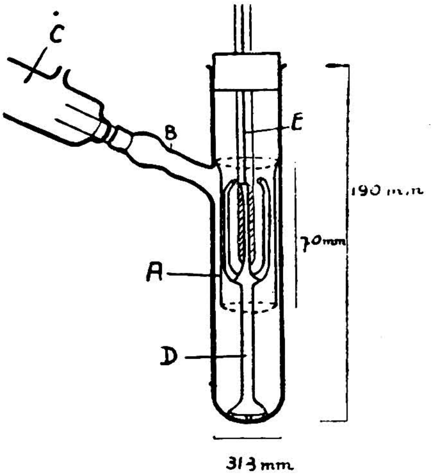


Fig. 1

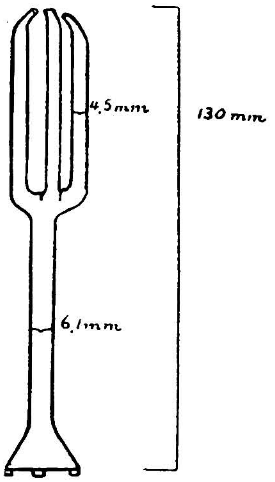


Fig. 2.

about an hour is required. Molecular weights between 100 and 200 are determinable with considerably less than the allowable 10 per cent. error, the only exception observed being that of *p*-nitrophenol in acetone, for which values of about 123·5 were repeatedly found, in place of 139·05. T. H. P.

Errata.—August issue. P. 455, 8 lines from bottom, *for* "action" *read* "cation"; p. 456, line 8, *for* "Ca" *read* "Ga."

Reviews.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. VIII. By J. W. MELLOR, D.Sc., F.R.S. Pp. x+1110. London: Longmans, Green & Co., Ltd. 1928. Price 3 guineas.

In this volume nitrogen and phosphorus only are discussed, and, of it, no less than 728 pages are devoted to nitrogen. The treatment is extensive and thorough, so much so, that many of the purely physical characteristics which lie almost entirely within the province of pure physics are included. Thus as regards air, which is treated in conjunction with nitrogen, the literature is reviewed appertaining to the physical aspects of liquefaction, the various types of spectra, thermal constants, speed of electrons in air, and the dielectric constant, and the text is replete with many physical constants and data.

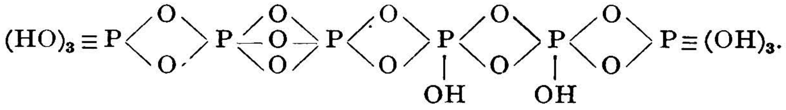
Dr. Mellor has made in this volume an innovation in that he has dedicated it "to the privates in the great army of workers in chemistry; their names have been forgotten; their work remains." These volumes of Dr. Mellor's will do much to perpetuate their names, and, although he has not acquainted us to any great extent with the results of their individual labours, evidently through limitations imposed by space, he has given us a general resumé of their work, and he has, moreover, by means of thousands of references, provided an invaluable key to their memoirs. Much might be written in favour of compilations of their own particular fields being made by specialists, but very often specialists are not to be enticed into such a form of activity, and for this reason chemists owe a considerable debt to Dr. Mellor, who has combined his wonderful ability and energy as a compiler, for supplying an urgent need. His remarkable volumes are destined to play a profound part in the development of physical and chemical science. The treatise is certainly the greatest which has yet been written.

The reviewer has previously commented on the curious nomenclature adopted in the treatise, and he cannot resist the temptation to call attention to it in respect of compounds described in the present volume. It is unnecessary and ugly, and a perusal of the names given in the index suffices to show how terrifying the system has become. It is extremely improbable that it will gain adoption, for it is unlikely that chemists will ever spare the time to fathom it. It serves no useful purpose to give names to products, whose individualities often have not been definitely established, especially when they are based upon their supposed nature. As an illustration, the hydrates of nitric acid may be quoted: $HNO_3.2H_2O$ is stated to be *orthonitric acid*; $2HNO_3.3H_2O$, *pyromesonitric acid*; $HNO_3.H_2O$, *mesonitric acid*; and $2HNO_3.H_2O$, *pyrometanitric acid*. Nevertheless, it is added that "there is but little satisfactory evidence of the polybasicity of these acids," and yet the author is led to deal with futile speculations that have been advanced, to the effect that certain basic nitrates are salts of either *orthonitric* or *metanitric acids*.

The complexity of the chemistry of nitrogen must have rendered its compilation difficult, and this must have been intensified by the dubious nature of much of that which has been written. The treatment accorded in the volume reveals that a good deal of the chemistry of nitrogen is, in all probability, in a very unhealthy state. One of the valuable effects of Dr. Mellor's work may be a revived interest, for the volume shows that the element provides a fruitful field for research.

The salient features of the reactions underlying the synthetic ammonia and nitric acid industries are briefly described. It might have been an advantage if greater space had been allotted to them, instead of, for example, the lengthy treatment given to the comparatively unimportant complex acids involving either ammonia or nitrogen pentoxide and the oxides of sulphur.

The reviewer disagrees with the attempts made in the volume to trace the constitution of the various acid phosphates to hypothetical polyphosphoric acids on the grounds of valency. The appropriate phase diagrams to be found scattered throughout the treatise show that their formation depends solely on the concentrations of the components and the temperature. It is irritating to find Thomas's Slag, probably a mixture of the secondary and tertiary phosphates of calcium, and whose composition approximates to phosphoric acid four-ninths neutralised, described as *calcium hexerohexaphosphate*, the salt of *hexerohexaphosphoric acid*, $H_8P_6O_{19}$, or



The volume has been published with the thoroughness exemplified in the foregoing volumes. Misprints are surprisingly few, though one, on page 958, attributes the value, $2{\cdot}7 \times 10^{-13}$, as having been found by the reviewer for the third dissociation constant of phosphoric acid, instead of $2{\cdot}7 \times 10^{-12}$.

HUBERT T. S. BRITTON.

THE CHEMISTRY OF CRUDE DRUGS. AN ELEMENTARY TEXTBOOK FOR STUDENTS OF PHARMACOGNOSY. By J. E. DRIVER and G. E. TREASE. Pp. 159. London: Longmans, Green & Co. Price 10s. 6d.

Not so many years ago the average pharmaceutical student could gain a fair knowledge of the chemistry of drugs in the course of his studies. In these days the case is different. Chemical investigation has opened up such large fields of knowledge of the alkaloids and terpenes, for example, that no student can hope to become familiar with more than a small part of this knowledge. It is, therefore, a problem for the writer of text-books to prescribe the amount of chemical knowledge that the student shall acquire, to select the most important ingredients, and to present them in a palatable and digestible form.

Up to a point, the authors of this text-book appear to have succeeded in this object. It is, however, questionable whether the numerous complex structural formulae will not be found somewhat indigestible by the student, who can hardly be expected to have the knowledge requisite for appreciation of the reasons for assigning these structures.

The book includes not only the chemistry of the active principles of crude drugs, but also the chemistry of other constituents, such as fatty oils, sugars and colouring matters. The difficulties of a rational classification of drugs are apparent. The authors have probably adopted as good a scheme as any that can be devised, but, even so, Musk, Insulin and Gelatin appear under the same heading. Some of the substances included, as will be gathered from those just mentioned, would be better classed as pharmaceutical materials than as drugs. A number of analytical notes are given as exercises for the student, chiefly qualitative tests, and a few quantitative determinations, such as saponification value, iodine value, etc., are described in a simple manner.

The term, arachic acid, is not so pleasing to the ear as the more common arachidic acid. The provision of a hitherto unknown rhyme to "Pharmacopoeia" in *Ipomoeia* (for *Ipomoea*) may bring the authors gratitude from some quarters. Otherwise the book is remarkably free from mistakes or misprints.

NORMAN EVERS.

THE EXTRA PHARMACOPOEIA. By MARTINDALE and WESTCOTT. Revised by W. H. MARTINDALE. Nineteenth Edn. Vol. I. Pp. xxxvi+1207. 1928. London: H. K. Lewis & Co. Price 27s. 6d.

The previous editions of this comprehensive manual have become so widely known to scientific workers in all parts of the world that a review of the general features would be redundant, whilst the wealth of information provided renders a detailed account impossible in these pages.

Since the last edition was published in 1924 (see review, ANALYST, 1925, **50**, 98), the text has been completely revised, and modifications and additions necessitated by the issue of several new National Pharmacopoeias have been included.

In addition, numerous investigations, described in a host of scientific periodicals both British and foreign, including several published as recently as the present year, have been briefly referred to or abstracted. The bulk of the volume steadily increases, and the present edition contains 44 pages more than the previous one, whilst the index (including references to Vol. II not yet published) contains considerably over 11,000 references to the text.

The value of the numerous data provided is greatly enhanced by the erudite and concise criticisms and suggestions of the reviser, whose wide knowledge of pharmaceutical and cognate matters renders these deserving of considerable respect.

An examination of the index indicates that Vol. II will contain material of more direct interest to the analyst; but the present volume, containing the chief physical and other properties of drugs, natural and synthetic, included in official and non-official materia medicas, the Poisons and Dangerous Drugs Acts of 1920, 1923 and 1926, notes on various foods, proprietary and otherwise, and the usual tables of metric equivalents, thermometric scales, atomic weights, etc., will be in frequent demand.

In the production of this work the authors have aimed high and achieved remarkable success, both in completeness and accuracy, and the volume deserves commendation to all pharmacists and chemists, to whom at one time or another it will prove invaluable.

T. J. WARD.

ORGANIC SYNTHESES. Vol. VII. FRANK C. WHITMORE, Editor-in-Chief. Pp. vii +105. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. Price 7s. 6d. net.

In the seventh volume of this series the characteristic features, by this time thoroughly familiar to all users of these books, are retained. Thirty preparations are detailed, the work of twenty-four contributors, four of whom are of countries other than the United States. Seventeen of the syntheses use, as raw materials, compounds described in this or earlier volumes. Among the substances described here may be noted: benzanilide, chloroacetamide, diphenic acid, furan, guanidine nitrate, and xanthone; the synthesis of one compound, anhydro-2-hydroxymercuric-3-nitrobenzoic acid, has never been published before.

A short appendix supplies some additions and corrections to preceding volumes; a collection of later references to preparations previously given will appear in Volume VIII.

A. F. KITCHING.