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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE ninth Summer Meeting was held at the Prince of Wales Hotel, Scarborough, from June 17th to 20th. The attendance, which included many ladies, was fifty-seven.

The Chairman (Prof. T. P. Hilditch) presided, and among those present were the following:—President (Prof. W. H. Roberts); Past Presidents (Dr. B. Dyer with Mrs. Dyer, Dr. J. T. Dunn with Mrs. Dunn, Mr. E. R. Bolton, Mr. J. Evans, Dr. Roche Lynch with Miss Roche Lynch and Mr. F. W. F. Arnaud with Mrs. Arnaud); Secretary (Mr. J. H. Lane); Mr. E. M. Hawkins, Miss Elliott and Miss Bradford; Scottish Section: Mr. A. R. Jamieson.

The Chairman cordially greeted the members, particularly those from the South and from Scotland.

On Saturday morning a paper was read by Dr. Roche Lynch, O.B.E., M.B., B.S., D.P.H., F.I.C., in which he related some strange coincidences which had come within his forensic experience, and also referred to the possible deleterious effects of the indiscriminate use of some of the new drugs and vitamin concentrates. A vote of thanks to Dr. Roche Lynch for his paper was proposed by Mr. C. J. H. Stock, seconded by Mr. F. W. F. Arnaud, and passed unanimously.

The President, in the name of the Parent Society, presented to Dr. Dyer one of the miniature badges which Past Presidents are entitled to wear, and took occasion to refer to the high esteem and affection in which Dr. Dyer is held. Dr. Dyer replied expressing his thanks.

A resolution, proposed by the Chairman and seconded by Mr. E. Gabriel Jones, was unanimously passed, expressing the continued loyalty and devotion of the North of England Section to the Council and the Parent Society.

A gift of roses was sent on behalf of the members to Mrs. W. H. Roberts as an expression of their sympathy in her illness.

On Sunday afternoon a motor run was made through rural scenery, and tea was taken at Lastingham, where the crypt of the Church was inspected.

The help of the following members in carrying out the arrangements is gratefully acknowledged:—Mr. W. G. Carey, Mr. A. Lees, Mr. C. Louden, Mr. T. W. Lovett and Mr. F. J. Smith.

Determination of Lead in Drinking Water

BY H. INGLESON, M.A., D.PHIL.

INTRODUCTORY.—It has long been recognised that some waters used for domestic supply attack the lead piping connecting the iron mains to consumers' taps and become contaminated with small quantities of lead. From time to time, cases of lead poisoning have resulted in many parts of the world and, in the localities affected, much work has been carried out in attempts to reduce the contamination and to form some estimate of the amount of lead which may be safely tolerated in drinking water. These aspects of the problem, and the theories advanced to explain the action of waters on lead, have been discussed in an earlier publication.[1]

In the present state of knowledge the extent to which a given water will be contaminated by lead piping under conditions of supply can be found only by direct experiment; it cannot be predicted with certainty from results of analysis of the water entering the lead pipe. This arises from the large number of variable factors, such as changes in the nature and concentration of the substances dissolved or suspended in the water, in temperature, and in the conditions of drawing the water from the piping.

Though it is recognised that there is some relation between the composition of a water and its action upon lead, the primary purpose of water analyses, as ordinarily carried out, is to ascertain the suitability of the water for drinking purposes and not to determine the probable action of the water upon lead or other metals. It is not surprising, therefore, to find that attempts to correlate the results of ordinary water analyses with the action on lead service pipes have been only partially successful. This point is well illustrated in a recent paper by Kruse[2] in which he gives the history of the serious outbreak of plumbism in Leipzig in 1930. After a detailed consideration of the large amount of data this author is unable to account satisfactorily for the outbreak of poisoning. The analytical results did not appear to show a change in the composition of the water sufficient to explain the change in its action upon lead, and Kruse concluded that some substance, not identified in the analyses, had made its appearance and had acted, possibly catalytically, in speeding up the rate of attack on the lead.

The Leipzig outbreak gave rise to legal proceedings by some 70 persons, and Fuchss, their legal representative during the five years of litigation, has collaborated with Bruns and Haupt in a review[2a] of the legal, medical and chemical aspects. These authors disagree with Kruse's catalytic theory of the cause of the epidemic. Since the cases arose in newly-erected blocks of flats, it is suggested that the new lead piping was, in large measure, responsible. They think it probable that changes in water composition had occurred, but that the analyses made during the relevant period were either not complete or not frequent enough to permit of a decision on the true cause of the excessive attack.

It is usually considered that hard waters have little or no action on lead, but some of these waters have, in fact, a marked action on the metal. For example, Beale and Suckling[3] have encountered several instances of very hard well waters, which were markedly plumbo-solvent and had given rise to lead poisoning, and they issue a warning against making the assumption that because a water is hard it is safe to convey it in lead pipes.

It seems certain that all waters under service conditions act upon lead piping, even after the lead pipe has been in use for some time, but that in many instances the amount of attack is so minute that it may probably be disregarded.

The wide distribution of lead, in small amount, in drinking waters from public supplies is discussed by Weyrauch and Müller,[4] who have determined the lead-content of waters in 21 German towns where no suspicion of plumbism had arisen. They found that traces of lead are by no means rare in water, particularly after it has been stagnant over-night in the lead pipes. They consider this to be the main source of the lead usually present in human bones. Many of the waters examined had a high temporary hardness and, though the amounts of lead were, in general, small, they were large enough to be detected readily by the usual analytical methods.

Many attempts have been made in the past to find out roughly at what point in the gradual transition from non-aggressive to aggressive waters the possibility of danger to health arises. This involves medical and chemical questions.[1] From the chemical side it may be said that the technique of analysing water for lead is fairly well understood and that the results obtained are reasonably accurate. It follows that, so far as the final chemical result is concerned, major importance attaches to the methods used in taking the samples for analysis.

In some areas of supply regular tests are made by the following method:—Specimens of bright lead are suspended in the water, with or without free access of air, for 12 or 24 hours, and at the end the lead in the water is determined. In other towns it is customary to determine the lead in the water after it has remained stagnant over-night in the service pipes; the values obtained by this method are generally assumed to represent maximum concentrations of lead likely to be encountered.* Whether the results obtained in this way do, in fact, represent maximum values is open to considerable doubt in the absence of direct experimental evidence.

The water (volume V) left stagnant in a pipe contains a limited amount of corrosive agent. The velocity of attack will be greatest in the early stages of contact when the concentration of the active agent is at a maximum, and it will fall with time, following a curve, the shape of which depends on the rate at which the active substance can reach the lead or otherwise assist the corrosion. On the other hand, the amount of corrosion, that is, the weight of lead changed from the metallic state, must increase with time to a limit dependent on the amount of active agent present. It is important to realise that the corrosion product initially formed may undergo change and may be precipitated on, and adhere more or less firmly to, the walls of the pipe. When, therefore, the volume of water V is withdrawn from the pipe after contact for *t* hours the amount of corrosion product passing out of the

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* In taking such samples it is desirable to have as large a volume of water as possible for analysis. At the same time it is important that the volume of water drawn off should not exceed the volume of the pipe between the tap and the iron street main, otherwise dilution with fresh water will occur. These apparently simple conditions are not always easily satisfied in practice because of the complications introduced by connections and by the uncertainty of the exact length of piping buried in the ground or under floors.

pipe with the sample is not necessarily equal to the total amount of corrosion product formed in t hours. The fraction of the total removed with the sample depends (*a*) upon the scouring action of the water during sampling, (*b*) upon the physical nature of the corrosion product, and (*c*) to some extent upon the relative positions of the tap and piping. In a vertical pipe the non-adherent corrosion product will tend to settle during quiescence to the lowest part of the pipe, and a sample of water taken at the base of the pipe may contain more lead than an equal volume of water removed from the top. Lead piping is bent in a very irregular fashion in fixing to house walls, and the bends may cause trapping of corrosion product. From what has been said it follows that the relation between the amounts of lead removed from a given tap in samples of water of volume V after times t_1, t_2, etc. cannot be stated in general terms, but must be determined by experiment. Very little information has been published to show how the length of the period of stagnation affects the lead-content of the samples of water.

The concentrations (p.p.m.) of lead in "stagnation" samples are not average values and cannot, therefore, when multiplied by the total volume of water ingested, give the total weight of lead taken into the body per day. Furthermore, there is very little published information to show how much water is used in the average household per person, per day, for drinking and cooking purposes only. Much information is available showing the overall requirements of each consumer, and in a recent paper before the American Waterworks Association, H. V. Pedersen[5] urged the desirability of finding out the fractions of the total consumption which were used in different ways. This would help in checking waste of water. He gives an instance of an American family of seven persons using 16·1 gallons per head per day for all purposes. Of this, he sets aside 5 per cent. for drinking and another 6 per cent. for cooking and kitchen work. For drinking and cooking, about 1·6 gallons per head per day were used.

Observations have been made by Magee[6] in two Public Assistance Institutions in England of the daily water ingestion of adults. The figures obtained are much smaller than Pedersen's results. The volumes used for drinking, in beverages, soups, stews, puddings, etc., averaged 0·616 gallon per day for men and 0·635 gallon per day for women. These values are in general accord with my observations on one household.

Since water plumbism is a chronic condition arising from the ingestion of small amounts of lead over an extended period, it is important, in attempting to correlate incidence of the disease with the lead-content of drinking water, to have a means of measuring the amount of lead removed from a given water-pipe over a period of time long enough to give a true average result. In the following paragraphs a method is described for determining the average concentration of lead in water withdrawn from household services over long periods. The method has been developed as a result of experiments carried out for the Water Pollution Research Board.

EXPERIMENTAL.—In the average household, water is withdrawn at irregular intervals of time and in varying amounts. From the outset the apparatus had to be designed for use by the housewife in the kitchen. The principle of the method is simple. Each small charge of lead present in the water drawn for consumption (*i.e.* for drinking or cooking purposes) is taken up by a bed of filtering material,* and at the end of the test the total accumulated lead can be found. The sum of the corresponding small volumes of water is obtained from readings of a water meter. The average lead-content of the water consumed can thus be readily determined.

For many years past filters have been used to protect consumers at times when a suspected contamination of a water supply was causing apprehension, but they have not hitherto been used as an aid to the analysis of water. The active media in these protective filters have been very varied in character; sand,[7] charcoal,[8,9] kieselguhr,[10] several types of coke[8] and calcium phosphate[11] have all been used. Small amounts of lead can be removed from solution by a large variety of substances, *e.g.* filter-paper,[12] peat and peat charcoal[13] and ferric hydroxide.[14]

In translating the simple principle of the method into practice, attention had to be given to the following points:—The filtering medium selected must (*a*) remove the whole of the lead, (*b*) have a high total capacity for lead, (*c*) not introduce any harmful or objectionable matter into the water being filtered, and (*d*) give the minimum of trouble in the final analysis. The filter itself must admit of ready replacement at the end of the test and, since the co-operation of the housewife is needed, it is important to ensure the greatest possible simplicity in operation, a good rate of flow, and that the apparatus is as compact as possible.

In the preliminary experiments the suitability of different materials as filtering media was judged by placing them in glass tubes and passing dilute aqueous solutions of lead salts through them until lead began to appear in the filtrate. When tested in this way, cotton-wool and filter-paper were found to be unsuitable for use under the conditions of the average household. Earlier work carried out in this laboratory[15] had shown that lead can be readily adsorbed from solution by base-exchange materials ordinarily used for water softening. It therefore appeared that they might be used, in a finely powdered condition, for the removal of both dissolved and particulate lead from water. If only the lead could be recovered subsequently from the filter by appropriate regeneration, a convenient method of sampling could be devised. Experiment showed that, though lead could be readily removed from solution, it was impossible to recover it quantitatively from the zeolite by the methods commonly used in regeneration of base-exchange materials. In one instance, which will serve as an illustration of the general behaviour, a total volume of a 5 per cent. sodium nitrate solution some 60 times the bulk volume of the base-exchange material was used in regeneration. Of the 100 mg. of lead known to be present in the zeolite, successive volumes of 500 ml. of the nitrate solution removed 1st, 40·3; 2nd, 7·9; 3rd, 3·4; 4th, 3·2; 5th (stationary contact), 5·4 mg., making a total of only 60·2 mg. A further 13·0 mg. of lead could be removed by treating the zeolite with 500 ml. of 5 per cent. acetic acid, giving a total of 73·2 per cent. recovery. It may be noted that this incomplete removal of metals from zeolites on regeneration is not peculiar to lead. It is difficult to remove calcium, barium, etc. completely from zeolites even by prolonged and repeated regeneration. Probably this behaviour is more marked with lead than with

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* I am informed by Prof. T. Campbell James, of University College of Wales, Aberystwyth, that he has analysed water samples for lead by using cotton-wool to adsorb the metal from aqueous solution. In this way tedious evaporations are avoided.

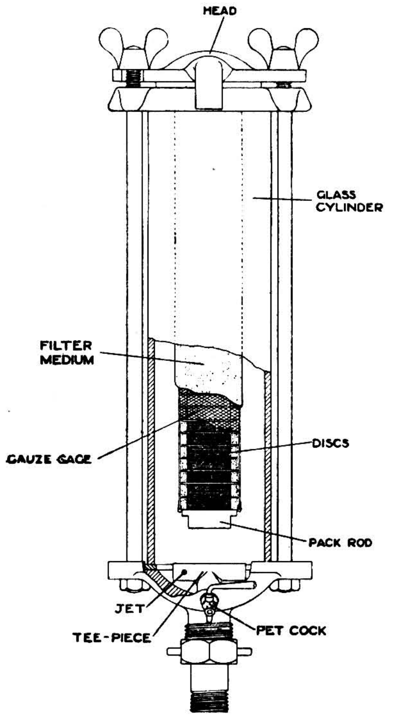

Fig. 1.

calcium because of the higher atomic weight of lead. It was obvious from the experiments that nothing short of complete disintegration of the zeolite would allow the recovery of the whole of the lead which had originally been removed from solution. The zeolites are materials of high silica-content and, since 70 to 100 g. of the substance would be required for each test, the removal of this silica would have involved long and tedious treatment during analysis. As sampling agents the zeolites were not, therefore, further considered.

Several kinds of refractory and other bricks and filter-candles were next tested, but the results were unsatisfactory, either because of the incomplete retention of lead or of the imperfect recovery of the metal from the adsorbent. One type of filter-candle used was found to be very fragile, whilst the method of jointing the body of another type to the collecting nozzle made it impracticable to treat the candle with acid solutions for the extraction of adsorbed lead. In addition, the rate of delivery of water under mains pressure was low.

Experiments were then made with a "Metafilter" domestic water filter. The principle of the apparatus has been explained by Pickard.[16] Though the type used in the experiments (Fig. 1) differs in detail from that described by Pickard, it admits of the formation, under pressure, of a compact layer of filtering medium, supported on a column of closely spaced metal discs. The method of operation is as follows:—The pack rod, with the head, is removed from the thick glass cylinder and the base of the filter is connected with the water supply. A suitable amount (varied according to the material) of finely powdered filter medium is then made into a thin cream with water (400 ml.) and poured into the cylinder. The pack rod is replaced and adjusted centrally by appropriate tightening of the winged nuts. When the water is turned on it passes at high speed through two small jets on opposite sides of the T-piece. An upward swirling motion is imparted to the suspended filter medium, which is deposited in an even layer between the plates and outside the removable gauze cage. If the material should deposit irregularly the water is shut off and the pet-cock is opened. This causes air to leak behind the plates, thus loosening the bed, which falls away from the cage. It can then be remade and the filter is ready for use. For the experiments described in this paper the great advantage of this type of apparatus over the compressed block or candle is that the nature of the filter medium can be changed or modified to suit the character of the water supply. When an experiment has been completed the filter material can be removed completely from the supporting pack rod and analysed for lead.

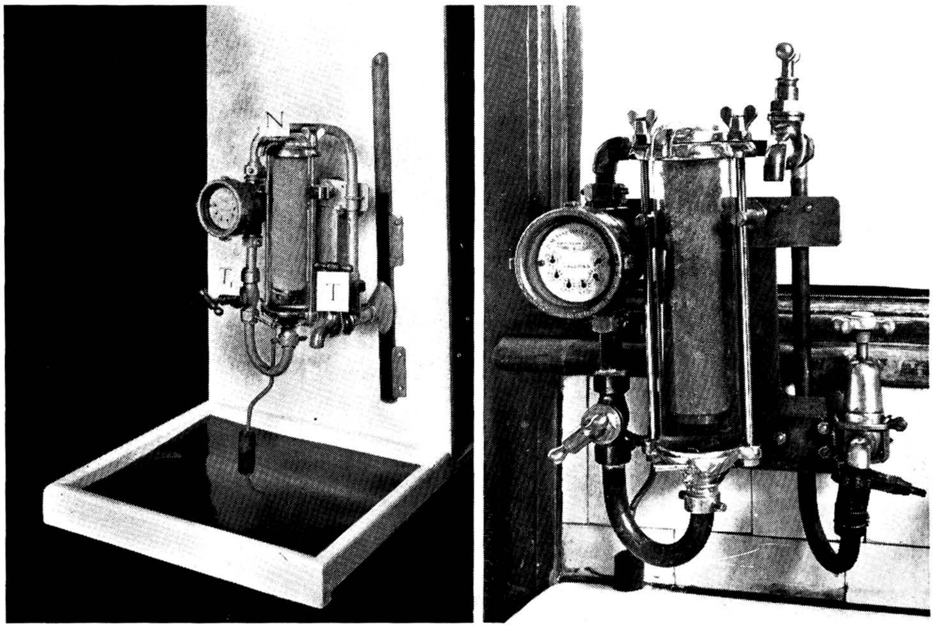

Fig. 2

Fig. 3

Two types of " Metafilter "

The tap T_2 in Fig. 2 is at the top on the right-hand in Fig. 3.

The photograph in Fig. 2 gives a general view of the complete apparatus. When water is required for consumption, tap T_1 is used. This allows water to pass through the meter and filter to be delivered from the nozzle N. Water for other purposes is taken from tap T_2.

In some towns it is the practice to solder the bib taps direct into the lead piping instead of screwing them into a brass tail-piece, which, as in Fig. 2, is soldered into the lead pipe. An alternative arrangement, shown in Fig. 3, can be used in such cases. Details of construction are shown in the scale drawing in Fig. 4.

The makers of the filter supply a special grade of kieselguhr for general purposes of filtration. When used to collect lead, kieselguhr gave rise to the same difficulty as had arisen with zeolites; the quantitative recovery of the lead was possible only when the material had been completely disintegrated. This involved the removal of 40 to 50 g. of silica during each analysis.

Activated carbon appeared to be a suitable alternative, since the finely-powdered material could be made to form a coherent bed after addition of a suitable binding agent, such as aluminium hydroxide. Carbon, however, gave trouble in the analysis because the lead was not readily extracted from it. The removal of the carbon involves burning it in air or oxygen, and during this process the temperature rises locally to over 1000° C. In these circumstances losses of lead oxide, which is appreciably volatile, cannot readily be prevented. In addition, trouble arises from the sintering of the ash left by the carbon and by the attack of lead compounds on the silica vessel in which the ignition is carried out.

Of the other finely-powdered, harmless, sparingly soluble substances readily available, magnesium oxide* seemed likely to give little trouble in analysis. Its absorptive power for lead was tested in the following way. A compact layer of the wet oxide was prepared on a Buchner funnel and a solution of lead nitrate was filtered through it. The lead in the filtrate was not sufficient to give a colour when tested with hydrogen sulphide.

A filter of the kind shown in Figs. 2, 3 and 4 was charged with 80 g. of magnesium oxide (heavy), and its mechanical behaviour was studied under working conditions in a local household. The main drawback to the use of the oxide was that after a few days the rate of delivery of the filtered water began to fall to such an extent that the apparatus was tedious to use. The graph (*a*) in Fig. 5 represents the general effect observed. Attempts to increase the rate of flow by the use of material of larger grain size were unsuccessful. The decrease had been caused by two factors: (1) Teddington tap water has a high temporary hardness (about 16 p.p. 100,000), and this brings about a deposition of calcium carbonate† between the grains of magnesia. The whole filter-bed becomes gradually transformed into a hard mass which, at the end of a month's use, is not easily removed from the pack rod; (2) deposition of ferric oxide, silica and small amounts of suspended

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* During this investigation Höll[17] published an interesting account of the conditions of water supply in Heligoland and of the outbreak of water plumbism on the island. He developed the use of burnt magnesite as a protective agent for use in percolating filters. Our observations confirm his statement, that magnesium oxide is an efficient absorbent for dissolved lead.

† In this connection it is interesting to note that the solubilities (g.-mols. per litre) given in Abegg's *Handbuch d. anorg. Chem.*, II (2) are $CaCO_3$ $0{\cdot}5 \times 10^{-4}$; $MgCO_3$ approx. $9{\cdot}5 \times 10^{-3}$; $Mg(OH)_2$ $1{\cdot}5 \times 10^{-4}$.

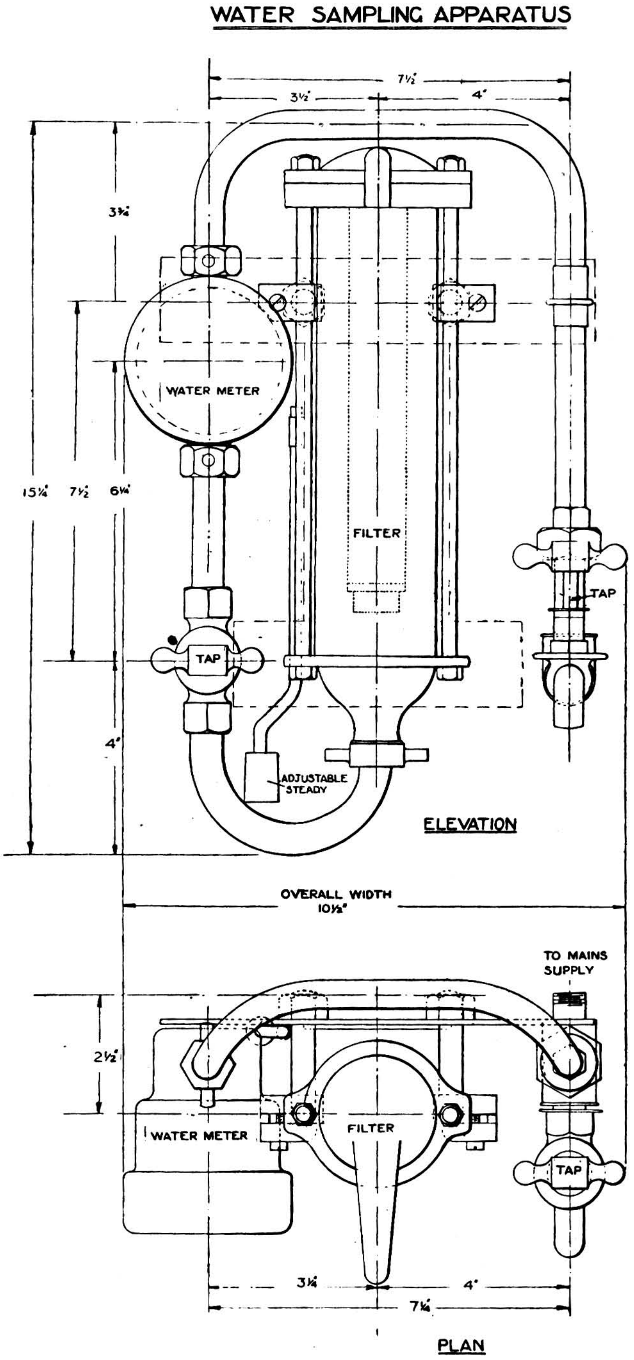
WATER SAMPLING APPARATUS
7½"
3½"
4"
3¾"
15¼"
7½"
6¼"
WATER METER
FILTER
TAP
TAP
4"
ADJUSTABLE STEADY
ELEVATION
OVERALL WIDTH 10½"
TO MAINS SUPPLY
2½"
WATER METER
FILTER
TAP
3¼
4"
7¼
PLAN

Fig. 4

matter picked up by the water during distribution. With the Teddington supply the second of these factors is of minor importance.

Since calcium carbonate was being deposited from the water it appeared that, by using this substance in the form of chalk, the major cause of the decreased rate of filtration could be removed. When chalk was used trouble was experienced with turbid water from the persistent presence of particles of chalk in the filtered water. After the water had been turned off the bed began to fall away from the cage, and when the water was turned on again more turbid water was obtained. It was decided to make use of the ability of magnesium oxide to remove calcium carbonate from the tap water and thus to bind the chalk grains into a reasonably compact filter-bed capable of remaining in position after the flow of water had ceased. It was found that a mixture of 10 per cent. of MgO and 90 per cent. of $CaCO_3$ not only formed a coherent bed but also that the filter would allow water to pass, after three weeks' use in a household, at practically the same rate as at the beginning. This is shown in Fig. 5, graph (*b*).

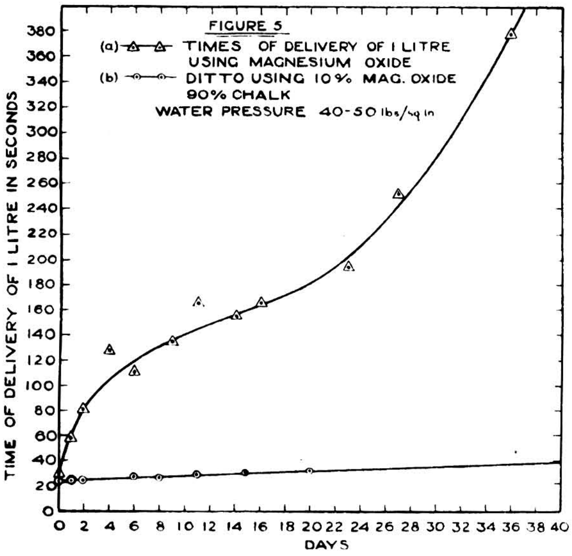

Fig. 5

Chalk in admixture with magnesium oxide removed suspended and dissolved lead compounds from water so completely that the filtrate gave no colour with hydrogen sulphide.

The mechanism of lead removal by calcium carbonate has not been studied fully, but it seems not unlikely that the very low solubility of lead carbonate, $PbCO_3$, and of the basic carbonate, $Pb_3(CO_3)_2\ (OH)_2$, which Pleissner[18] gives as corresponding to 0·04 mg. of lead per litre, may cause a small amount of calcium of the chalk to replace the lead in solution. The solubility product* of lead carbonate ($PbCO_3$) would be $3{\cdot}3 \times 10^{-14}$, whilst that of calcium carbonate is $2{\cdot}74 \times 10^{-9}$. Since the concentration of carbonate ion will remain constant, in the presence of the large excess of chalk, at $5{\cdot}23 \times 10^{-5}$ it follows that the con-

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* Abegg's *Handbuch d. anorg. Chem.*, 1909, Vol. III, (2), 726.

centration of the lead cannot exceed $6{\cdot}3 \times 10^{-10}$ mols. per litre or 0·00013 mg. per litre. If this view of the mechanism is correct it supplies a ready explanation of the absence of lead, as shown by the test with hydrogen sulphide in the filtrate from the chalk. Cooper[19] has estimated that the sensitivity of the sulphide test for lead is 1 part of metal in 100 million to 196 million parts of water according to the conditions of the test. The first of these values corresponds with 0·01 mg. of lead per litre, or about 80 times the amount calculated as in equilibrium with the calcium carbonate—lead carbonate mixture.

ANALYTICAL.—Some of the problems of analysis of samples of water and excreta for lead have already been discussed.[1] The difficulties arise in general from the smallness of the amounts of lead (rarely exceeding 1 mg.) to be determined. Such small amounts of lead are usually associated with 0·5 to 1 g. of other materials in a large volume of water. To ensure, in these circumstances, the quantitative separation of lead from other metals requires special technique which must be varied according to the conditions.

With the filter already described it is possible to obtain an appreciable quantity of lead from a large volume of water (hundreds of gallons if necessary) and to analyse the filtering medium by well-established methods. In the filtering material in some tests the amount of lead has been as high as 200 mg. The result is that the small gains or losses of lead incidental to analytical procedure are relatively unimportant. A disadvantage of the method is that the lead is mixed with 50 to 100 g. of the filter material.

It is only necessary to deal here in detail with the methods of analysis adopted when magnesium oxide or mixtures of it with chalk were used as filter media, because the use of the other materials introduced such difficulties in the analysis that determinations were both too lengthy and too tedious to form the basis of a satisfactory method.

Magnesium Oxide.—After use in the filtration of 50 to 200 gallons of a tap water the magnesium oxide contains, besides lead, calcium carbonate, silica, oxides of iron, small amounts of copper and organic matter. The analysis of the material has therefore to be undertaken in two sections: (*a*) on the portion soluble and (*b*) on that insoluble in dilute hydrochloric acid. The soluble portion, containing about 80 g. of the oxide in solution together with the bulk of the lead, is treated so as to separate the metal from most of the extraneous matter; the organic matter and silica in the insoluble fraction are removed by wet oxidation by nitric and sulphuric acids and treatment with hydrofluoric acid. The residue, freed from sulphuric acid, can then be united with the main solution at a suitable stage in the analysis. The tests to find the most suitable analytical procedure for concentrating the lead present in portion (*a*) were made by adding known weights of lead (as nitrate) to 80 g. of magnesium oxide before dissolving the oxide in hydrochloric acid. On making the solution, diluted to 1 litre, slightly acid with hydrochloric acid and treating with hydrogen sulphide only about 60 per cent. of the lead was recovered. This is in accord with the observations of Dede and Bonin[20] that high concentrations of neutral chlorides hinder and, in some instances, prevent completely the precipitation of lead sulphide from hydrochloric acid solution.

The second procedure tried was that used by Allport and Skrimshire[21] and is based on the observations of H. Fischer,[22] that lead produces a brilliant red compound with solutions of diphenylthiocarbazone in organic solvents such as chloroform. By mechanical separation of this solution the lead can be concentrated. When applied to magnesium oxide the process gave an excellent recovery of the added lead; for example, of 109 mg. of lead, added as lead nitrate, 108 mg. were recovered. The method therefore appeared likely to solve the problem of separating the lead, but it should be pointed out that calcium carbonate is present in the oxide after use and so, to be of service, the extraction must be quantitative in the presence of calcium salts.

Magnesium Oxide with Chalk.—The application of the method of Allport and Skrimshire to solutions made by dissolving 110 g. of a mixture of chalk and magnesium oxide (MgO 10 per cent., $CaCO_3$ 90 per cent.) in hydrochloric acid gave unsatisfactory results.* In most instances the lead recovered did not exceed about 15 per cent. of that known to be present. The reason for this marked difference in the presence of calcium salts is not clear and was not investigated, since other methods were tried with success. Two further methods of initial precipitation were tried, namely, the separation of lead as the carbonate by addition of sodium carbonate to the nitric acid solution of the mixture and the removal of the lead as the chromate from the nitric acid solution rendered neutral by addition of ammonia. Both methods gave a satisfactory recovery but, whereas the addition of sodium carbonate brought down a considerable amount of calcium carbonate the potassium chromate merely precipitated the lead in admixture with the small quantity of magnesium hydroxide produced during neutralisation of the nitric acid solution. The chromate method is therefore preferred because less unwanted material is precipitated, and because it possesses the advantage of giving a preliminary rough idea of the quantity of lead present.

The next step in the analysis consists in precipitating the lead (and any copper) as the sulphide from hydrochloric acid solution. This separation, besides removing traces of alkaline earths, prevents the precipitation with the lead, in the later stages of analysis, of any manganese that may be present.

The next stage consists in dissolving the sulphide in hot dilute nitric acid and then depositing the lead as peroxide on the anode by electrolysis in nitric acid solution. The deposition of manganese in this way was shown by Luckow[23] in 1880.

The lead can then be determined gravimetrically as the sulphate or, if very small in amount, colorimetrically as the sulphide.

Details of analysis of filter material after use.—After being used in a test the whole of the filter material is transferred to a 4-litre beaker with the minimum volume of water. Owing to its length and weight it is convenient to place the filter pack in a glass pie-dish (10·5 × 6·5 × 2·0 inches) during the removal of the medium from the metal framework. Conc. nitric acid is gradually added until just enough acid has been used to ensure the solution of all save the brown or black flocculent matter which floats about even after several hours' gentle boiling.

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*It should be pointed out that Allport used this reagent for determining lead in samples of dyestuffs in which the total amount of mineral matter was of a different order of magnitude from that employed in the experiments described in this paper.

The filtrate and washings from this solution (A) are allowed to cool, and the solid matter and filter-paper are oxidised with conc. sulphuric and nitric acids to yield a residue (B), which is set aside for a later stage.

To solution A (approximately 2 litres) is added ammonia until a faint permanent opalescence is seen; 200 ml. of 1 per cent. potassium chromate solution are added to produce a yellow cloud of lead (and copper) chromate. The boiled, cooled solution is filtered by suction through a fritted Jena glass filter (17G.4) from which, after washing, it is dissolved by warm dilute hydrochloric acid and boiling water. The resultant solution is repeatedly taken to dryness with conc. hydrochloric acid until no further evolution of chlorine occurs, and the solid is then boiled with water to yield solution C. At this stage a second residue of silica often remains; this is added to residue B for treatment with hydrofluoric acid. The residue from this treatment with hydrofluoric acid consists principally of calcium and magnesium sulphates with small amounts of the lead salt. After the removal, by evaporation, of the excess of sulphuric acid the residue is united with solution C in a 2-litre conical flask; 1 ml. of conc. hydrochloric acid is added, and the solution is diluted to 1 litre. If there are indications that very little copper is present a small amount of copper (50 to 100 mg.) is added as sulphate to ensure the proper coagulation of lead sulphide. In order to hinder the production of colloidal sulphur during the precipitation of the lead and copper as sulphides it is convenient to use the following procedure:—The acidified solution is boiled for 5 to 10 minutes, and while the liquid is still boiling the flask is transferred to an asbestos mat. A rubber bung carrying a glass tube, which reaches about 2 or 3 inches into the flask, is loosely inserted into the neck of the flask. A stream of washed hydrogen sulphide is passed into the flask, which is gently agitated. The steam released and the gas together expel any residual air, and when the bung is firmly pressed into position the current of gas continues as the pressure in the flask falls with the gradual cooling of the solution. The sulphides separate in a clear liquid which, after passage through a fritted glass filter, gives a filtrate free from suspended sulphur. Any small residue of sulphides adhering to the flask is removed by boiling dilute nitric acid (30 ml. of conc. acid per 100 ml. of solution) added after hydrogen sulphide has been expelled by boiling a small amount of water in the flask. This hot acid is used to dissolve the main portion of the sulphides; the solution is evaporated, and nitric acid is added to bring the free acid concentration to that recommended by Francis, Harvey and Buchan.[24] The solution is electrolysed under the conditions of temperature and voltage which these workers recommend, and the lead which separates as the peroxide is then determined gravimetrically (as sulphate) or colorimetrically (as sulphide).

Tests with the filter.—Tests of the ability of the filter medium itself to remove lead from water had already been made, so that it remained only to test the operation of a filter charged with the medium. To operate satisfactorily, the filter requires a considerable head of water. This head was obtained by placing a bell jar on a laboratory roof and passing a current of water from it through 56 ft. of glass tubing to the filter at ground level. To this water stream a solution of lead of known concentration was slowly added. Before each test, water was allowed to run to waste for about 15 minutes. The water providing the head in the bell jar was obtained from a rising lead main, 1 inch in diameter, supplying a storage tank; though the pipe might be expected to influence the lead-content of the water, its replacement by an iron one was impracticable. The retention of the lead pipe, though causing some inconvenience during the tests, was well justified by the discovery of a phenomenon hitherto unsuspected.

The results obtained in these tests are shown in Table I.

TABLE I

	Lead added g.	Lead recovered g.	Difference g.
(1)	0·1467	0·1473	+ 0·0006
(2)	0·2052	0·2038	— 0·0014
(3)	0·0535	0·0562	+ 0·0027
(4)	0·0618	0·0637	+ 0·0019

Investigation showed that no significant amounts of lead were obtained from (*a*) the filter medium, (*b*) the apparatus, (*c*) the water in the iron mains. The lead-content of the water from the rising leaden main was examined, with the results shown in Table II.

TABLE II

	Blank Tests	Lead found g.
(1)	Filter medium used as in Table I, no lead added ..	0·0075
(2)	Water from *top* of pipe after stagnation over-night ..	0·00064
(3)	Repeat of No. 2	0·00061
(4)	Water stagnant over-night in lead main removed, after closing main valve, from *base* of pipe	0·0056
(5)	Repeat of No. 4	0·0034

The results in Table II, in which from 5 to 9 times as much lead is obtained from the base as from the top of the pipe, may be explained on the assumption that slight disturbances, due to vibration or thermal changes, occur in the 56 ft. of vertical pipe. These disturbances cause small particles of "protective" layer to become detached from the walls of the pipe, and, being specifically heavier, to collect in the lower part of the pipe. These particles are unlikely to be removed from this pipe except by prolonged flushing.

A second series of tests, made after the pipe had been flushed out for four to five hours before each test, gave the results in Table III.

TABLE III

	Lead added g.	Lead recovered g.	Difference g.
(1)	0·1752	0·1712	— 0·004
(2)	0·1562	0·1583	+ 0·0021
(3)	0·2845	0·2886	+ 0·004
(4)	0·1383	0·1398	+ 0·0015

In a blank test the same filter-bed was used on 5 successive days to collect the lead left after flushing out for 4 hours each day. This resulted in the collection of 0·0074 g. of lead.

Two conclusions can be drawn from these experiments:

(1) that the filter removes dissolved and suspended lead quantitatively from the water;

(2) that in sampling drinking water for lead adequate attention should be paid not only to the length of the piping but also to its spatial disposition.

Meters.—The meters used in the apparatus illustrated in Figs. 2 and 3 were of the displacement type and were tested under conditions of actual use, *i.e.* by filtering a series of irregular amounts of water until 10 gallons had been recorded on the units dial. Some results are given below.

Meter	Volume of water delivered when 10 gallons recorded	Error Per Cent.
A	9·74	+ 2·6
B	9·82	+ 1·8
C	9·68	+ 3·2
D	9·78	+ 2·2
E	9·74	+ 2·6

Results of household tests.—The subjoined Table IV, giving a selection of results obtained in tests made in households in different parts of the country, is included to illustrate the amounts of lead found in practice.

TABLE IV

Site	Period of year	Period of test (Days)	Volume of water passed through filter		
			(Gallons)	$PbSO_4$ g.	Pb p.p.m.
A	October	27	36	0·0254	0·106
	Dec.–Jan.	34	35	0·0210	0·090
	Jan.–Feb.	40	43	0·0240	0·084
	March	20	21	0·0082	0·059
	April–May	23	21	0·0125	0·090
	Aug.–Sept.	31	33	0·0194	0·088
B	Sept.–Oct.	31	29·5	0·0120	0·061
C	October	13	33	0·0090	0·041
	Dec.–Feb.	61	100	0·0027	0·004
	Feb.–April	71	182	0·0150	0·012
	April–June	54	150	0·0106	0·010
D	Dec.–Feb.	61	245	0·0150	0·009
	Feb.–April	71	278	0·0094	0·005
	April–June	54	144	0·0148	0·015
E	Feb.–April	71	22	0·0394	0·270
F	April–June	54	114	0·0968	0·127
	June–Sept.	92	70	0·0602	0·129
	Sept.–Nov.	82	72	0·0362	0·078
G	Oct.–Jan.	42	42	0·0374	0·134
	Jan.–April	63	148	0·1050	0·106
	April–June	48	65	0·0926	0·214
	June–July	42	82	0·1866	0·279

TABLE IV—*continued*

Site	Period of year	Period of test (Days)	Volume of water passed through filter		
			(Gallons)	$PbSO_4$ g.	Pb p.p.m.
H	Jan.–April	69	168	0·0590	0·053
	April–June	64	131	0·040	0·046
	June–July	46	184	0·1586	0·129
	July–Nov.	69	111	0·043	0·058
I	Jan.–March	59	188	0·3978	0·317
	March–June	74	71	0·2484	0·526
	June–Aug.	72	277	0·5824	0·315
	Aug.–Nov.	87	273	0·1775	0·094

SUMMARY AND CONCLUSIONS.—A new method is described for finding the average lead-content of water used in a household for drinking and cooking. By means of the apparatus the housewife can draw water for these purposes at such times during the day as it is required. A filter abstracts the small amounts of lead from the water while a meter records the sum of the small volumes used over a period of several weeks. In this way it is not only possible to sample the water under actual conditions of use but also to eliminate the irregularities associated with "snap" sampling. The weight of lead to be determined is so very much greater than that present in snap samples that an analytical separation of the lead can be made. It is thus possible to avoid the use of analytical devices commonly employed to prevent interference with colour tests by other metals during the determination of minute amounts of lead.

The assistance courteously extended by a number of water engineers has enabled tests to be made, under a variety of conditions, at pressures ranging from 40 to 100 lbs. per sq. in. and with waters of widely differing characteristics. The purpose of the experiments made has been to develop and improve a method of sampling for lead and thus facilitate the carrying out of the main objective—that of trying to correlate the attack on lead piping with the character of the water and other conditions of supply.

The investigation described in this paper was carried out as part of the programme of the Water Pollution Research Board.

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An Investigation into the Methods of Toxicological Analysis of Viscera

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PART II. THE EXTRACTION OF ALKALOIDS FROM VISCERA

INTRODUCTION.—In Part I of this investigation[1] an attempt was made to separate and consider each point of difficulty in the classical Stas-Otto process of determining alkaloids in viscera, and as a result a modified method was devised which, tested on quinine and morphine, gave satisfactory results. We have satisfied ourselves, moreover, that, with the technique advocated, as good results can be obtained from experiments on animals injected with the required alkaloid as from experiments involving the simple addition of alkaloid salts to minced viscera. Accordingly, in this part of the investigation, the experiments were confined to those involving this addition of alkaloid salts to minced viscera. This is more particularly advisable, since the alkaloids now dealt with are easily hydrolysed and, under the influence of metabolic processes, undergo comparatively rapid degradation. Hence, the percentage of such alkaloids recovered in an animal experiment would yield little information on the efficiency of a recovery process.

Subsequent to the sending for publication of Part I of this investigation, Stewart, Chatterji and Smith[2] published some work on the subject on lines similar to those we have followed and to the experiments published by Peltzer.[3] Their method consists essentially in precipitation of the proteins with trichloroacetic acid, adsorption of the alkaloid with kaolin, and its elution with chloroform or ether after being rendered alkaline with sodium carbonate and dried with sodium sulphate. During this process even easily hydrolysable alkaloids are subjected to the action of hot conc. sodium carbonate solution, which does not appear to be very desirable. As stated previously, we discarded adsorption and elution processes largely owing to the lack of adsorbing power of the materials used in the presence of comparatively large amounts of strong electrolytes. In addition, moreover, we found that, under the conditions of quantitative adsorption and elution, the resulting alkaloid was always contaminated with a by no means negligible amount of biological extractives, which involved a subsequent rigorous purification of the isolated alkaloid. We have now tried trichloroacetic acid as a protein precipitant and find that the resulting coagulated protein has a somewhat rubbery consistence and so does not, in our opinion, lend itself to washing and draining as readily as the more granular precipitate produced by ammonium sulphate. In general, in our hands, trichloroacetic acid has given lower results than ammonium sulphate.

We have endeavoured to prove the general applicability of the method described by us (*loc. cit.*) by determining the efficiency of the process for the recovery of strychnine, cocaine, atropine and aconitine. These, together with quinine and morphine, the two alkaloids originally selected, provide a range of alkaloids varying in their behaviour with immiscible solvents and in degree of stability to hydrolytic agents. It will be agreed, we think, that this range is sufficiently general for it to be assumed that all other alkaloids will behave similarly.

One of the fundamental requirements of the Stas-Otto process is the utilisation of a series of solvents, petroleum spirit, ether, chloroform, etc., to effect a separation of any mixture of alkaloids. Such a separation may be necessary, but we consider it essential to isolate, in the first place, the mixture of alkaloids in a fairly pure state. Accordingly, we have modified our original process so as to be applicable to all alkaloids. Experiments with the further additional alkaloids specified have shown that morphine is unique in being extracted from tissue by saturated ammonium sulphate solution. All the other alkaloids are extracted to only a small extent by 1 to 1·5 litre of this solution. Accordingly, in any general scheme, the extraction medium must be acidulated water. Again, chloroform is the only solvent which dissolves all alkaloids, with the exception of morphine, which requires special treatment.

GENERAL METHOD.—The general method of extraction of alkaloids from viscera finally adopted is as follows:

(i) Freeze the tissue overnight in the ice compartment of a refrigerator.

(ii) Mince 400 g., or other suitable quantity, into a tared casserole while the material is still frozen.

(iii) Add 50 ml. of water and 10 ml. of glacial acetic acid and warm, with stirring, to about 50° C.

(iv) Add sufficient ammonium sulphate (200–300 g.) to leave a small amount undissolved and warm, with stirring, to about 65° C.; the protein will then have coagulated and the thick gruel will have become quite fluid.

(v) Filter on a large Buchner funnel and wash with about 100 ml. of warm water (65° to 70° C.).

(vi) Return the residue to the casserole, macerate at about 65° to 70° C. with approximately 200 ml. of water containing 1 per cent. of acetic acid until the mixture has been stirred into a thin gruel free from lumps and filter.

(vii) Repeat the maceration of the residue with hot acidulated water until approximately 1·5 litre of total filtrate has been obtained.*

(viii) Transfer this filtrate to a 2-litre separating funnel and render alkaline with ammonia. Extract five times with 100-ml. portions of chloroform and filter the chloroform extracts.

(ix) Unite the filtered chloroform extracts and extract successively with 25, 15 and 10-ml. portions of 3 *N* sulphuric acid, followed by 25 ml. of water, and filter the aqueous extracts in turn through a small filter.

(x) Render the united aqueous liquors alkaline with ammonia, extract with five 20-ml. portions of chloroform, and filter into a small carbon dioxide flask.

(xi) Evaporate the colourless extract to dryness in the flask and weigh.

(xii) Dissolve the contents in a little dilute acid and filter the solution through a small paper. Wash the flask and paper well with dilute acid (if necessary, the washings can be left separate from the main bulk of concentrated alkaloid solution).

(xiii) Return any small amount of insoluble matter on the filter to the flask by dissolving it in acetone and then in chloroform. Dry and re-weigh the flask, the difference from the previous weight representing the weight of pure alkaloid.

This general method serves for all alkaloids except morphine. For that alkaloid, 200 ml. of alcohol are added after (vii) above and extraction is repeated with chloroform and alcohol. If morphine only is sought, however, it is preferable to adhere to the method given in Part I.

There are a few points which require amplification:

(*a*) The mixing of the ammonium sulphate extract with the water extracts causes a turbidity. No attempt must be made to filter this. The admixture must, however, be made, since, with certain alkaloids, the amount dissolved by the ammonium sulphate solution, though small, is not negligible.

(*b*) If the heating of the tissue with ammonium sulphate is not sufficiently thorough, or, if the material is abnormal in behaviour, possibly owing to disease, persistent emulsions in the chloroform layer are formed on extraction. This need cause no delay. The chloroform emulsion is filtered through a small Buchner funnel containing a filter-paper with a half-inch layer of acid-washed sand on top; this breaks the emulsion. Subsequent extractions are run through the same funnel, so that only a small washing with chloroform is needed at the end to free the funnel and its contents from alkaloid.

(*c*) Filtration of the chloroform and aqueous liquors at every stage is essential for securing a high-grade product at the termination of the experiment, even though it is not apparently necessary.

(*d*) With the technique as finally evolved it is unnecessary to remove any traces of fat from the acid filtrate, since the fat remains in the first chloroform extract.

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* For quantities of tissue weighing as little as 200 g. the volume of dilute acetic acid used for extraction may be reduced somewhat, but we make it a practice to finish with not less than 1 litre of extract. The quantities of chloroform used subsequently are not altered.

(*e*) Too much stress cannot be laid on the necessity of confirming, where possible, the purity of the alkaloid returned as "yield" in quantitative work of this nature.

EXPERIMENTAL.—In the experiments described below the alkaloid was added in aqueous slightly acidulated solution to the minced material prior to its acidification with acetic acid.

The "standard method" referred to in the following tables is the general method described above :

TABLE V

QUININE EXPERIMENTS

50 mg.* of alkaloid used in each experiment

Expt.	Material	Yield of quinine Crude Per Cent.	 Purified Per Cent.	Remarks
27	Liver, 400 g. + 50 ml. of blood	89	86	Standard method. Purified by precipitation as tartrate.
28	Liver, 400 g. + 50 ml. of blood	92	84	Standard method, except that the material was macerated with water acidulated with trichloroacetic instead of acetic acid.
29	Liver, 400 g. + 50 ml. of blood	86	56	Protein coagulated with 50 g. of trichloroacetic acid in 50 ml. of water and material macerated with water acidulated with trichloroacetic acid.

* Quinine weighed as quinine hydrate and dissolved in a minimum of hydrochloric acid prior to addition to minced material.

N.B.—Compare the result in Expt. No. 27 with those in Expts. Nos. 7 and 11 (Pt. I).

TABLE VI

STRYCHNINE EXPERIMENTS

50 mg.* of alkaloid used in each experiment (except No. 35)

Expt.	Material	Yield of strychnine Crude Per Cent.	 Purified† Per Cent.	Remarks
30	Liver, 350 g.	99	78	Mass extracted with a total of 1·5 litre of saturated ammonium sulphate solution (27 per cent. yield), followed by extraction with a total of 1·5 litre of acidulated water (51 per cent. yield). Emulsions not broken by sand.
31	Liver, 340 g.	—	77	Standard procedure. Emulsion not broken by sand.
32	Liver, 340 g.	—	89	,, ,, ,, ,, ,, N.B.—The chloroform extraction is incomplete if the emulsions are not broken. The loss naturally depends on the type of emulsion.
33	Liver, 400 g.	—	115	As Expt. 30. Recovered strychnine crystalline but straw-coloured and slightly impure, even after recovery as ferrocyanide.
34	Liver, 350 g.	—	93	Standard procedure. Strychnine, dry colourless crystals.
35	Liver, 350 g. + 5 mg. of strychnine		mg. 6·5	Standard procedure. Strychnine, dry pale straw-coloured crystals.

* Strychnine weighed as free base and dissolved in a minimum of hydrochloric acid prior to addition to minced material.

† The yield represents the amount of alkaloid recovered after purification by precipitation as ferrocyanide (4).

TABLE VII

COCAINE EXPERIMENTS

50 mg.* of alkaloid used in each experiment (except Nos. 39, 40)

Expt.	Material	Yield of cocaine Per Cent.	Remarks
36	Liver, 350 g.	56	Liver somewhat diseased rendering filtration difficult. Filtrate made alkaline with $NaHCO_3$ and cocaine extracted with petroleum spirit throughout. Final product readily and completely crystallisable. Petroleum spirit gave very persistent emulsions which rendered complete extraction impossible.
37	Liver, 400 g.	84	As Expt. 36, but ether used in place of petroleum spirit.
38	Liver, 350 g.	85	Standard procedure; chloroform used as solvent and emulsion broken with sand. Cocaine solidified to mass of pale brownish crystals.
39	Liver 350 g. + 5 mg. of cocaine	mg. 2·7	As Expt. 37, ether used. Yield not satisfactory.
40	Liver, 400 g. + 5 mg. of cocaine	5·7	Standard procedure. Cocaine solidified to thick pasty mass of crystals.

* Cocaine weighed as cocaine hydrochloride and dissolved in acidulated water prior to addition to minced material.

N.B.—The cocaine was extracted with petroleum spirit, instead of chloroform, from the final acid liquor to increase the purity of the product. In each experiment microscopical and chemical tests were made on the final product.

TABLE VIII

ATROPINE EXPERIMENTS

50 mg.* of alkaloid used in each experiment (except No. 44)

Expt.	Material	Yield of atropine		Remarks
		Crude Per Cent.	Purified† Per Cent.	
41	Liver, 400 g.	72	—	Standard method, except filtrate made just alkaline with $NaHCO_3$. The solution was probably not sufficiently alkaline to obtain complete extraction.
42	Liver, 400 g.	97	79	Standard method.
43	Liver, 400 g. + 50 ml. of blood	89	—	Standard method, except that material was macerated with water acidulated with 1 per cent. of trichloroacetic instead of acetic acid.
44	Liver, 400 g. + 5 mg. of atropine	mg. 7	—	Standard method. Product gave strong reactions in all the characteristic chemical tests.

* The atropine was weighed as sulphate and dissolved in water prior to addition to the minced material.

† The atropine was purified by precipitation with Wagner's reagent and weighed as hydriodide-octaiodide (5).

TABLE IX

ACONITINE EXPERIMENTS

Expt.	Material	Yield of crude aconitine Per Cent.	Remarks
45	Liver, 400 g. + 50 mg. of aconitine*	75	Standard method. The yield was low, as this was a preliminary experiment. Repetition not considered necessary owing to low poisonous dose. Final product formed resinous mass which crystallised from ether in fine colourless needles.
46	Liver, 400 g. + 5 mg. of aconitine*	mg. 6·0	Standard method. Gave characteristic chemical and physiological tests.
47	Liver, 400 g. + 0·5 mg. of aconitine*	mg. 4·2	Standard method. General chemical alkaloidal tests strongly positive. Physiological tests positive. The crude alkaloid† was dissolved in 10 ml. of acidulated water. 1·0 ml. of the solution was diluted again to 10 ml. with water, and four rats were injected intraperitoneally with 1·5, 2·5, 2·5, 3·5 ml. respectively of this solution. The rat receiving 3·5 ml. died in 1½ hours; one of the 2·5 ml. rats died at end of 24 hours. The other two recovered after severe symptoms of aconitine poisoning.

* Aconitine weighed out as hydrobromide and dissolved in acidulated water prior to addition to minced material.

† *Cf.* Discussion of Results, *infra.*

DISCUSSION OF RESULTS.—The results obtained show that the modified method of extraction of alkaloids from viscera described here is suitable for the determination of quinine, strychnine, cocaine, atropine and aconitine. The method has, throughout, been treated as a routine method, and the experiments quoted are typical experiments. Without doubt, by taking extreme precautions, such as extracting the minced material with further quantities of acidulated water from which the alkaloid is extracted separately, and by further exhaustive extraction of all the solutions obtained, the yield of alkaloid could be increased. It is doubtful, however, whether this is worth while when the quantity of alkaloid present is small. In those experiments involving 5 mg. of alkaloid it will be noticed that the quantity of alkaloid weighed approximates closely to the actual quantity present, the amount of adventitious matter being only 1·5 to 2 mg. In Experiment 47 the adventitious matter is slightly more, owing to an attempt to avoid loss of alkaloid. It may be pointed out that good yields depend on removing completely each chloroform extract before re-extraction. The advantage of breaking any residual emulsion by filtering through sand under suction is due to the complete separation of the chloroform layer obtained by this method.

We have tested the method of Stewart, Chatterji and Smith (*loc. cit.*), though not exhaustively, because we have had, so far, greater success with our method.

Work is in progress to adapt our method to the determination of synthetic drugs, such as the barbiturates, amidopyrin, etc.

SUMMARY.—A modified method of extraction of alkaloids from viscera is described which is suitable for any alkaloid. It has been demonstrated that good yields can be obtained and that the amount of contaminating adventitious material is small.

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The Determination of Aluminium in Cast Iron

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INTRODUCTION.—At the present time no reliable method is available for the determination of aluminium in cast iron and ferro-alloys. The literature so far published on the subject is at variance as to the merits of existing methods. Thus, Lundell, Hoffman and Bright[1] regard the phosphate method as inaccurate, but not sufficiently so to exclude it for routine analyses. Ibbotson[2] gives this particular method as the best, whilst Naish and Clennell[3] suggest its use for the determination of small amounts of aluminium only, and recommend precipitation as hydroxide by means of sodium thiosulphate in reduced solution for larger amounts of the element.

A survey of the published literature shows that the phosphate method, which is probably that most widely used to-day, was first introduced by Stead[4] in 1889; a subsequent slight modification by Carnot[5] appeared in 1891. In present-day literature this method differs only in very slight detail from the original, and it is obvious from a study of the methods of 50 years ago that it was devised to deal with the small amounts of aluminium remaining in steel after the addition of the element as a deoxidant.

In view of the rapidly increasing importance of aluminium as an alloy addition to cast iron, and the consequent need for its accurate determination in comparatively large amounts, an investigation of the existing methods has been carried out. Special attention has been paid to the use of 8-hydroxyquinoline, a reagent recently introduced into inorganic analysis by Berg[6] and his co-workers. It has been found that this reagent may be used under certain conditions, which are given in detail later (p. 587), for the determination of aluminium in cast iron and ferro-alloys, and the results obtained are of a high standard of accuracy, both for small (0·05 per cent.) and large (14 per cent.) amounts of the element.

This investigation has occupied a period of more than twelve months, and every detail of the method subsequently given has been carefully studied and the conditions of precipitation verified by numerous determinations carried out on both synthetic solutions and samples of cast iron containing aluminium. The effects of other alloying elements, such as nickel, copper, chromium, molybdenum, etc., as well as titanium and vanadium, have also been examined in the same manner.

THE SEPARATION OF ALUMINIUM FROM IRON.—The primary difficulty encountered during the determination of aluminium in ferrous materials is its separation from the large amounts of iron associated with it. There are numerous methods in use at the present time for achieving this object, as follows:—(1) the Rothé ether separation; (2) the sodium hydroxide separation; (3) the precipitation of aluminium as phosphate in reduced solution; (4) the precipitation of aluminium as hydroxide in reduced solution; (5) the removal of iron by precipitation with hydrogen sulphide in ammoniacal tartrate solution; (6) the sodium bicarbonate separation; (7) electrolysis with a mercury cathode.

All these separations, with the exception of the last, have been studied in detail, and it appears that none is entirely satisfactory when used singly for amounts of aluminium in excess of 1 per cent. A combination of the bicarbonate separation and the ammonium sulphide—tartrate separation has proved to be the most satisfactory.

The Rothé ether separation, introduced by Rothé[7] in 1882, is tedious and exacting. Its success depends upon the sp.gr. of the test solution, since a solution of sp.gr. 1·100 to 1·105, saturated with ether, retains the smallest amount of ferric chloride. It cannot be employed as an absolute separation, as some iron is invariably left in the aqueous layer. Considerable experience is necessary to obtain satisfactory results with this separation.

Precipitation of the aluminium as phosphate in reduced solution is regarded by many of the later writers as unreliable, as previously stated, and the present investigation has shown that this is undoubtedly correct. With very small amounts of aluminium the error may be negligible for routine purposes, as stated by Naish and Clennell,[3] but for the determination of more than 0·5 per cent. of aluminium the method is very unreliable. Further, it is subject to serious interference from such elements as titanium and vanadium, which are frequently present in cast iron. Chromium also causes interference, and no entirely satisfactory method of removing it from the precipitated phosphates, except in very small quantity, has yet been devised. Titanium and vanadium may be removed by fusion of the mixed phosphates with sodium carbonate, but this procedure renders the method long and tedious and the final result even more uncertain.

Precipitation as hydroxide in reduced solution may be accomplished by means of either sodium thiosulphate, as recommended by Naish and Clennell,[3] or phenylhydrazine, recommended by Hess and Campbell.[8] Both these methods have been examined. The former yielded only about 75 per cent. of the aluminium present, whilst the latter failed to separate the large amount of iron present. If, however, the bulk of the iron present was removed by one of the other separations, the latter method yielded as good results as could be expected from a hydroxide method.

The hydrogen sulphide separation in ammoniacal tartrate solution[28] shows greater promise. It has the disadvantage that samples of more than 1 g. cannot be conveniently handled, owing to the unwieldly bulk of the iron sulphide precipitate obtained, but for separating less than 1 g. of iron it is absolutely quantitative, though the statement of Gadeau,[9] that the iron sulphide does not adsorb aluminium, appears to be incorrect if more than 1 per cent. of that element is present. The same writer[9] states that the precipitated sulphide filters and washes well, but this statement also appears to be erroneous, for although a great variety of filter-papers has been tried, the iron precipitate was found to filter and wash very badly indeed unless not more than 20 mg. of iron was present. This difficulty was subsequently overcome by fractionation, as will be seen later. This separation has the advantage of removing other elements, such as manganese and nickel, together with the iron. Lundell, Hoffman and Bright[10] state that the separation of manganese and nickel by this method is incomplete, but the amount remaining in the solution after filtration is of the order of 0·1 mg., and is therefore negligible.

The sodium hydroxide separation is stated by Lundell, Hoffman and Bright[11] to give low results, and Lundell and Knowles[12] suggest that this is due to the retention of aluminium by the precipitated ferric hydroxide. This is rather to be expected, as the adsorbing properties of ferric hydroxide are well known, and the present work has confirmed this fact. The difficulty may be largely overcome by making a second sodium hydroxide separation after dissolving the first precipitate in acid, but this is inadvisable, since by so doing large quantities of sodium salts (probably more than 20 g.) are introduced into the final solution, and their presence is objectionable.

The sodium bicarbonate separation has proved to be valuable for separating the aluminium present from most of the iron prior to the use of one of the other separations. It removes about 90 per cent. of the iron present and a similar proportion of the manganese. The precipitate contains, in addition to aluminium and a little iron and manganese, any titanium, vanadium, chromium, copper, tin or phosphorus which may be present at the time of precipitation.

In order to study the various methods for the precipitation of aluminium in synthetic solutions, with or without the addition of iron or other elements (such as titanium, chromium, etc.) several standard solutions were prepared.

Standard Aluminium Chloride Solution.—The basis of this solution was a sample of aluminium metal supplied by the Royal School of Mines, and its chemical analysis was as follows:—aluminium, 99·70; silicon, 0·13; iron, 0·15; total, 99·98 per cent.

The solution was prepared by dissolving 4·2000 g. of this aluminium metal in 40 ml. of 50 per cent. hydrochloric acid, diluting, filtering and making up the volume of the resulting solution to exactly 2000 ml.; 50 ml. of this solution were theoretically equivalent to 10·50 mg. of aluminium. This value was repeatedly checked by several modifications of the oxine method and was found to be 10·30 mg. per 50 ml. of solution. The filtrates from these check determinations were tested for aluminium by the colorimetric method of Lampitt and Sylvester,[14] but none could be detected, thus proving the completeness of the precipitations.

Iron.—For the additions of iron, a sample of "Powdered Iron" was employed; its chemical analysis was as follows:—iron, 99·65; carbon, 0·10; manganese, 0·17; silicon, trace; phosphorus, 0·01; sulphur, 0·03; titanium, nil; vanadium, nil; chromium, nil; total, 99·96 per cent.

The preparation of other standard solutions is described later under the headings of the appropriate elements.

THE PRECIPITATION OF ALUMINIUM AS HYDROXIDE AND SUBSEQUENT IGNITION TO OXIDE.—The aluminium, having been successfully separated from the iron associated with it, it becomes necessary to decide by what method the solution shall be treated to obtain the final result. At the present time precipitation with ammonium hydroxide, followed by the ignition of the precipitate to aluminium oxide, is extensively employed. This method, however, is open to serious objection. In the first place, precipitation with ammonium hydroxide needs careful manipulation if correct results are to be obtained. The *p*H of the solution is of great importance; the minimum solubility range of aluminium hydroxide lies between the limiting *p*H values 5·7 and 6·3.[13] Thus an excess of ammonium hydroxide must be avoided; the use of methyl red as an indicator for this purpose is to be strongly recommended, since its yellow colour is developed at *p*H 6·4.

For the precipitation of small amounts of aluminium an excellent procedure has been evolved by Lampitt and Sylvester[14] and is carried out as follows:—The solution containing the aluminium is treated with a very slight excess of ammonium hydroxide and it is then boiled until the vapours no longer smell of ammonia. These authors[14] state that "this is the most important part of the procedure and is the only point where serious error can be made. The excess of ammonia must be removed, otherwise an appreciable loss of aluminium will occur. On the other hand, if the boiling is unduly prolonged, the solution becomes distinctly acid and the aluminium re-dissolves." This procedure has been extensively used during the present investigation for the testing of precipitates for adsorbed aluminium and for testing filtrates to ensure that precipitation has been complete. Such tests were completed by the colorimetric method, using aurintricarboxylic acid, as described by Lampitt and Sylvester.[14]

Thus, by careful control of the *p*H of the solution, the whole of the aluminium may be precipitated with ammonium hydroxide. When the materials, such as cast iron, contain phosphorus, this element is precipitated, completely or in part, together with the aluminium. Titanium is similarly precipitated. It is therefore necessary to determine the amount of phosphorus in the precipitate and to deduct its equivalent of P_2O_5 from the weight of aluminium hydroxide,[15] etc., recorded, if ignition to oxide is chosen as the method for the final determination. The presence of titanium necessitates the fusion of the precipitate with anhydrous sodium carbonate and the removal of the titanic acid so obtained after extraction in water.

The procedure of ignition to oxide is, however, by no means satisfactory, except for the determination of small amounts of aluminium (up to 0·5 per cent.). First, it is very difficult to ignite the hydroxide completely to oxide, since it retains its elements of water very tenaciously and, further, the ignited alumina is very hygroscopic and is therefore difficult to weigh accurately. The present investigation has shown that results obtained by this method are invariably high, quite apart from any interference due to phosphorus or other elements. Numerous precipitations were made from pure aluminium solutions with ammonium hydroxide, and the precipitates so obtained were ignited in platinum crucibles at temperatures ranging from 1000° to 1450° C. The results are shown in Table I, and it will be seen that the figures are still above the theoretical, even after ignition at the highest temperature. Although the plus error is small, being of the order of 0·6 mg., it is by no means negligible, since it represents an error of 0·06 per cent. of aluminium if samples of 1 g. are employed. For larger amounts of aluminium the error would become more and more serious, especially if samples of 0·5 g. or less are employed. For this reason, together with the fact that the procedure for estimating phosphorus or for removing titanium renders the process long and introduces greater possibilities of error, the method is not one to be recommended for the determination of aluminium in cast iron or any other alloy.

TABLE I

Aluminium in synthetic solution	Weight of Al_2O_3 obtained and corresponding weight of Al					
	Ignition temp. 1000° C.		Ignition temp. 1250° C.		Ignition temp. 1450° C.	
mg.	Al_2O_3 mg.	Al mg.	Al_2O_3 mg.	Al mg.	Al_2O_3 mg.	Al mg.
20·00	38·9	20·58	38·7	20·48	—	—
10·30	21·0	11·11	20·9	11·07	—	—
10·00	20·0	10·58	19·9	10·54	—	—
10·00	20·4	10·79	20·3	10·74	19·9	10·54
10·00	20·4	10·79	20·3	10·74	19·9	10·54

PRELIMINARY EXAMINATION OF HYDROXYQUINOLINE METHODS.—8-Hydroxyquinoline, or oxine, is a light buff-coloured crystalline solid, m.p. 73° to 75° C. It forms insoluble complexes with certain metals by substitution of its phenolic hydrogen atom. These compounds are characterised by their definite constitution, their stability, and their crystalline, easily filterable form; they are believed to be either chelate or co-ordination compounds. Further, owing to the high molecular weight of the organic part of the molecule, these compounds are very voluminous and heavy; this means that they contain only a small percentage of the metal, and thus results are of a high standard of accuracy, and further, small amounts of metal give rise to large precipitates, so that traces may be readily detected and determined. These remarks are of special interest when considering aluminium, which is a tervalent metal of comparatively low molecular weight and consequently combines with three mols. of oxine to give $(C_9H_6ON)_3Al$, which contains only 5·88 per cent. of aluminium.

Solvents.—The reagent is insoluble in cold water, but comparatively soluble in hot water, from which it may be recrystallised, if necessary, for purposes of purification. It is also soluble in alcohol, acetone and acids. For general purposes an alcoholic solution is used, but for the determination of aluminium this is impracticable, since the aluminium oxine complex is itself slightly soluble in this solvent. The alcoholic solution will keep only for a few days, but an acetic acid solution is stable for a period in excess of one month.

8-Hydroxyquinoline was introduced into quantitative analysis about 1927. Its use is described by Berg,[6] Hahn and Vieweg[17] and Robitshek.[18] These early researches dealt with the determination of such elements as copper, aluminium, cadmium, bismuth, zinc and magnesium in pure solutions. Later workers[12] have shown that the reagent may be employed to separate aluminium from such elements as phosphorus, vanadium, titanium, arsenic, molybdenum, uranium, fluorine, boron, beryllium and tantalum, provided that suitable conditions are established.

Conditions of Precipitation.—In acetic acid solution the following elements are precipitated completely or in part:—silver, lead, mercury (bivalent), copper, bismuth, cadmium, antimony (tervalent or quinquevalent), uranium, iron (bivalent or tervalent), zinc, manganese, cobalt, nickel, aluminium, zirconium, niobium, tantalum, chromium and vanadium (quadrivalent or quinquevalent).

In ammoniacal solution all the above-mentioned elements yield precipitates except silver, and, in addition: beryllium, magnesium, calcium, strontium, barium and tin (quadrivalent or bivalent).

Contrary to statements made in previous literature,[19] precipitation of small amounts of aluminium can be made in very dilute hydrochloric acid solutions containing ammonium chloride.[27] Tartrates, however, must be absent. Under these conditions no precipitation of manganese occurs, but chromium is partly precipitated. Amounts of aluminium in excess of about 5 mg. cannot be precipitated by this method, because the amount of acid required to hold the aluminium in solution (in the absence of tartaric acid) renders the solution too acid to allow precipitation to take place. It will be seen that aluminium may be precipitated either in acetic acid or ammoniacal solution in the presence of tartrate.

Since the reagent forms precipitates with so many metals, it would at first appear that it would be useless for the present purpose. But most of these elements are either easily removed, or are seldom encountered in ferrous materials in sufficient quantity to cause serious interference. Thus, mercury, lead, bismuth, copper, cadmium, and antimony are readily removed by hydrogen sulphide in acid solution, whilst iron, zinc, manganese, nickel and cobalt are removed by the same reagent in ammoniacal tartrate solution. The remaining elements, with the exception of titanium, vanadium and chromium, which have received special attention in this investigation, are as yet unlikely to be encountered in cast iron.

Precipitation with oxine has the advantage that the metallic complexes may be dissolved in mineral acid and titrated with a solution of potassium bromate containing potassium bromide, followed by the titration of the iodine, liberated by adding potassium iodide, with sodium thiosulphate. Provided that suitable precautions are taken, this volumetric completion has been found to give results as accurate as the gravimetric method and it reduces the time required for a determination very considerably. The final procedure is given later, together with the reasons that led to its adoption. During the titration the oxine is quantitatively brominated to its 5: 7-dibromo-derivative, in accordance with the following equation:

$$C_9H_7ON + 2Br_2 \longrightarrow C_9H_5ONBr_2 + 2HBr$$

In the early part of this work the gravimetric method was first employed and then the precipitates were dissolved in acid and titrated. This proved a valuable check on the volumetric method, since weighed amounts of the oxine complex were being determined. Later the volumetric ending was employed alone, but from time to time a gravimetric result was obtained as a check.

Drying Temperature of Oxine Precipitates.—The various writers on the gravimetric oxine method are at variance as to the temperature at which the precipitate should be dried. Their recommendations vary from 100° to 160° C. In the course of the work which forms the subject of this paper the precipitates were dried at various temperatures between these limits without any appreciable change in the results obtained. Finally, a temperature of 105° to 110° C. was adopted as being most convenient, and all precipitates have been dried at this temperature for one hour and then re-heated to constant weight at the same temperature. In every instance the weights were constant after the first hour, except with precipitates weighing more than 0·7 g., when a period of 1·5 hours at 105° to 110° C., or 1 hour at 135° to 140° C., was necessary.

The first method of precipitation to be studied was the hydroxyquinoline method of Gadeau[9]:

> "A sample of 0·5 g. is dissolved in conc. hydrochloric acid (or sulphuric acid) and the solution is evaporated to dryness (or to fumes of sulphuric acid) to render silica insoluble. Without filtering off the silica, etc., 200 ml. of water are added, together with 5 g. of tartaric acid and sufficient ammonium hydroxide solution to render the odour of ammonia apparent. Then a rapid stream of hydrogen sulphide is passed through the solution for 20 minutes, after which the liquid is filtered and the precipitate is washed carefully with water saturated with hydrogen sulphide. The filtrate contains the whole of the aluminium without a trace of iron."

After boiling for some time to expel the excess of hydrogen sulphide the aluminium is precipitated as follows:

> "After the solution has been made slightly acid with acetic acid it is warmed to 50° to 60° C., and 10 ml. of an acetic acid solution (5 per cent. oxine in 12 per cent. acetic acid) are added. Then a little ammonium acetate solution (154 g. per litre) is added, drop by drop, until precipitation commences and then a further 20 ml. of the ammonium acetate solution. Under these conditions $(C_9H_6ON)_3Al$ is precipitated. After the solution has stood in a warm place for three or four hours it is filtered through a sintered glass filter, and the precipitate is washed with water containing a little ammonium acetate and dried for one hour at 140° to 160° C. The aluminium is weighed as $(C_9H_6ON)_3Al$."

$$\text{Per cent. of Al} = (C_9H_6ON)_3Al \times 0{\cdot}0588 \times 2.$$

After the precipitates obtained by this method had been weighed, they were dissolved in hydrochloric acid and titrated in accordance with the procedure given by Hopkin and Williams[16], which is as follows:

> "The precipitate is dissolved in a little warm conc. hydrochloric acid (the compound is not readily soluble in weaker acid), the solution is diluted with about five times its volume of water, and a little indigo carmine or methyl red solution is added. The solution is then titrated with $N/5$ bromine solution (5·567 g. of potassium bromate and 50 g. of potassium bromide dissolved in water and diluted to one litre) to a yellow colour. A few g. of potassium iodide are added, and the liberated iodine is titrated with $N/10$ sodium thiosulphate, using starch solution as indicator (1 ml. $N/5$ bromine solution $\equiv$ 0·0004495 g. Al).
>
> ". . . A simple direct titration with the bromine solution is not possible, since the indicators do not show a sharp end-point."

In order to study this method, varying quantities of the aluminium chloride solution already described (p. 568) were taken, thus:—100 ml. $\equiv$ 20·6 mg. Al; 50 ml. $\equiv$ 10·3 mg. Al; 25 ml. $\equiv$ 5·15 mg. Al. Some of the solutions containing only aluminium chloride were diluted to a volume of 300 ml., tartaric acid was added, and the precipitation carried out exactly as described in the method under examination. To other solutions varying amounts of iron (p. 568) were added, and the hydrogen sulphide separation was carried out; determinations were completed exactly as prescribed. Some of the results for these two series are shown in Table II.

It will be noticed that in every instance the results were lower than the known amount of aluminium. In some, the figure is much lower (Expts. Nos. 3 and 4). Further, the volumetric results are occasionally much lower than the corresponding gravimetric figures (Nos. 2, 4 and 7).

After the weighed precipitates had been dissolved from the sintered glass crucibles a slight black residue remained, and an attempt was made to weigh this with a view to explaining the lowness of some of the volumetric results. It was found that the substance was little more than a stain, since no increase in weight could be detected after the crucibles had been dried to constant weight at 105° to 110° C. The true explanation was not found until a much later stage in the investigation (see p. 584).

TABLE II

Expt. No.	Aluminium added mg.	Iron added mg.	Weight of oxine complex obtained mg.	Aluminium obtained mg.	Aluminium from volumetric determination mg.
1	5·15	nil	85·2	5·01	4·86
2	10·30	nil	169·0	9·94	9·32
3	15·45	nil	247·2	14·52	14·40
4	10·30	1000	165·7	9·74	9·44
5	10·30	500	169·6	9·93	9·89
6	10·30	500	168·9	9·92	9·92
7	5·15	500	84·5	4·97	4·69
8	5·15	500	83·5	4·91	4·83

It was also noticed that, contrary to the statement of Gadeau, it was very difficult to filter off and wash the iron sulphide precipitate. In an attempt to overcome this difficulty, a large variety of filter-papers was employed, but without success. Finally, the following procedure, which avoids all washing of the precipitate, was adopted:—One-gram samples were taken, instead of the recommended 0·5 g., and dissolved in hydrochloric acid; the hydrogen sulphide separation was carried out as before, and then the precipitate and solution were transferred to a 500-ml. graduated flask, diluted to the mark, and well mixed. After the precipitate had settled somewhat, 250 ml. were filtered off into another graduated flask through a Whatman No. 1 filter paper (18·5 cm.). This 250-ml. portion (0·5 g. of the sample), was transferred to a beaker, and, after evaporation to 100 ml., it was acidified with hydrochloric acid, and sufficient bromine water was added to colour the solution yellow. The excess of bromine was expelled by boiling, the solution was rendered ammoniacal and then just acid with 30 per cent. acetic acid (litmus paper as indicator), and the aluminium was precipitated with oxine as before.

The bromine was added because it had previously been noticed that when boiled to remove hydrogen sulphide, the solution deposited sulphur, and it was necessary to remove this before proceeding with the gravimetric determination. The sulphur can, of course, be filtered off after concentration of the liquid to a very small bulk, but the use of bromine is more reliable and saves much time.

The results obtained by this method were closely similar to those already given in Table II, and, therefore, inconsistencies observed must have been due to some other factor.

Precipitation in Ammoniacal Solution.—Since it is stated in the published works on the oxine methods that the element titanium is precipitated in acetic acid solution, together with vanadium, precipitation in ammoniacal solution seemed to offer greater promise than the previous methods for the determination of aluminium in cast iron. The procedure examined was that published by Lundell and Knowles,[12] and is as follows:

> "To the solution slightly acid with either sulphuric or hydrochloric acid, and containing not more than 0·1 g. of aluminium in 100 ml. volume, add an excess of 2·5 per cent. solution of 8-hydroxyquinoline in dilute acetic acid (made by triturating 2·5 g. of oxine with 5 ml. of glacial

acetic acid and pouring the solution obtained into 100 ml. of water at 60° C.; after cooling, the solution is filtered) and then dilute ammonium hydroxide solution until the solution is alkaline, and finally an excess of 5 ml. of strong ammonium hydroxide per 100 ml. of solution. Warm to 60° C. to 70° C. and digest at this temperature until the precipitate becomes dense and crystalline. Cool, preferably in iced water, and filter, washing with a cold dilute solution of ammonium hydroxide (1 : 40) containing 25 ml. of the reagent, previously neutralised with ammonium hydroxide, per litre."

The above-mentioned authors complete their determinations by destroying the organic matter in the precipitates by treatment with conc. sulphuric and nitric acid and then precipitating the aluminium as hydroxide with ammonium hydroxide and igniting to oxide. In view of the difficulties and drawbacks of this latter procedure, already mentioned, the precipitates obtained during this investigation were filtered off on sintered glass crucibles, dried and weighed. To do this successfully it was necessary to omit the addition of the reagent to the washing medium.

When titanium and vanadium are present, Lundell and Knowles recommend the procedure described, with the addition of 10 ml. of 20 vol. hydrogen peroxide prior to the addition of the oxine solution.

This method was studied by using the same aluminium chloride solution as before, and adding titanium as a standard solution prepared in the following manner:—*Standard Titanium Solution.*—Pure titanium oxide (0·8324 g.) was fused with 10 g. of potassium bisulphate at a dull red heat. The fused mass was extracted in 200 ml. of 5 per cent. sulphuric acid; it was found that sometimes the titanium salt tends to be hydrolysed during extraction; if this occurs, the solution should be evaporated until fumes appear, when the precipitated titanium will redissolve. The solution was then diluted to 1 litre. (1 ml. ≡ 0·0005 g. of titanium).

The results obtained by precipitation are shown in Table III, and it will be seen that they are lower than those obtained in acetic acid and acetate solution. This may be due to filtration difficulties, for it was found that, whereas the precipitates obtained in acetic acid and acetate solution are bright yellow in colour and coagulate readily on standing, and consequently are easy to separate, those obtained in ammoniacal hydrogen peroxide solution turn a dark brown colour on standing and are difficult to filter off and wash. The solution also turned deep red, and all attempts to coagulate the precipitate failed. Owing to these difficulties, precipitation in ammoniacal solutions containing hydrogen peroxide was abandoned after numerous experiments on solutions containing no iron.

TABLE III

Expt. No.	Aluminium added mg.	Titanium added mg.	Aluminium found mg.
9	5·15	nil	4·84
10	5·15	nil	4·93
11	5·15	nil	4·76
12	5·15	2·0	4·84
13	5·15	2·0	4·74

In view of the fact that neither of the two oxine methods studied yielded satisfactory results, it was decided to endeavour to correlate results for aluminium determinations obtained by the oxine method of Gadeau and the standard phosphate method on samples of cast iron. The phosphate method is given in detail at a later stage.

The results obtained by the phosphate method and the oxine method are shown in Table IV, and it will be seen that they are far from satisfactory, since both methods yield inconsistent figures.

TABLE IV

Sample No.	Aluminium by phosphate method				Aluminium by oxine method			
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
6781		2·20	2·17		2·20	2·08	2·10	2·12
6782		4·84	4·76		4·82	4·93	4·72	4·82
6780	7·51	7·46	7·72	7·57	6·98	6·99	7·04	7·13
					7·27	7·22	7·05	7·16
					7·45	7·39	7·35	7·35
6797		8·85	9·31		8·44	8·07	8·30	8·29
6762		5·90	5·85		4·72	4·96	5·12	5·84
6761		5·76	5·90		5·76	4·20	4·87	
6783		6·94	6·62		6·28	6·28		
6758		3·88	3·76		3·92	3·91	3·93	

For example, with sample 6780, twelve oxine determinations were made, and only one pair agree among themselves (7·35, 7·35), whilst the phosphate figures vary by 0·3 per cent. With 6761 the variations are even greater for the oxine method. For sample 6758 the oxine figures agree well, but those by the phosphate method are much lower. The only instance where reasonable agreement is shown between the two methods is the 2 per cent. aluminium sample 6781, and it is a significant fact that the differences become greater as the aluminium-content of the samples increases. It was subsequently found that all the oxine figures given above were low. In view of these irregularities, a complete study of both methods was begun. The investigations were carried out simultaneously, but for the sake of clarity the phosphate method is dealt with first.

THE PHOSPHATE METHOD.—As stated at the outset, the phosphate method has altered little during the last fifty years. The details of the first method examined are as follows[20]:

> "Weigh out 2 g. of the sample, dissolve in 20 ml. of conc. hydrochloric acid and keep the solution as free from oxidation as possible. Filter off the graphitic carbon, silica, etc., and to the filtrate add dilute ammonium hydroxide until a permanent precipitate is obtained, then add 10 ml. of sulphurous acid and boil. Add 2 g. of sodium phosphate, followed by ammonium carbonate solution until a faint permanent precipitate appears; just redissolve this precipitate in conc. hydrochloric acid and add 2 ml. in excess. Then add 20 ml. of 30 per cent. acetic acid, make the volume of the solution up to about 300 ml. and heat to boiling. Next cautiously add 10 g. of sodium thiosulphate, a small amount at a time, until a precipitate of sulphur appears, and then add the remainder. Boil the solutions until the vapour stream is free from sulphur dioxide (about 20 minutes), filter through a paper pulp filter and wash with hot water containing 1 per cent. of ammonium phosphate and nitrate. Transfer to a crucible and ignite at the mouth of the muffle furnace. Dissolve the precipitate in a small amount of conc. hydrochloric acid, heating if necessary, and filter off the insoluble matter. Add 1 g. of sodium phosphate, neutralise as before and make the final precipitation with 5 g. of sodium thiosulphate. Ignite the precipitate obtained at the mouth of a muffle furnace and weigh as aluminium orthophosphate, which contains 22·10 per cent. of aluminium."

This method was first applied to a series of pure aluminium chloride solutions, and later iron was added in varying amounts from 0·5 to 2·0 g. The results are shown in Table V, in which each number represents a duplicate determination, for which each figure is given. It will be seen that all the results are below the known amount of aluminium added. In spite of this, the weights of aluminium phosphate obtained after two precipitations are in very close agreement; this is the most serious difficulty yet disclosed, since, in the normal course of routine analysis, all the results given in Table V, with the exception of No. 22, would be accepted as correct, although they are actually in error to the extent of from 0·05 to 0·15 per cent. The results for Nos. 21 and 22 are examples of those in which the phosphate method failed to precipitate more than about 10 and 20 per cent. respectively of the aluminium present; no explanation for this could be found, since as far as possible the conditions of precipitation were identical with those in the preceding experiments. It will be noticed, of course, that the weights of the first precipitates show a large increase as soon as iron is introduced, but this is of no consequence, since it has long been known that some iron is invariably precipitated at this stage.

The writers of literature published on this method are at variance as to the correct ignition temperature for the final precipitate. Thus Ibbotson[2] states that a temperature of 600° C. should not be exceeded, whilst Lundell, Hoffman and Bright[1] recommend 1000° C. as the correct temperature. In the present series of tests the precipitates were first ignited at 600° C. and then reheated at 1000° C. for 30 minutes, and a study of the resultant figures given in Table V shows that no appreciable change in the weights occurs. Thus it appears that either temperature may be employed without vitiating the results.

In explanation of the fact that the phosphate method gives inconsistent results, several writers have suggested that the phosphate $AlPO_4$ is formed only when a definite proportion of Al_2O_3 to P_2O_5 is present, and Naish and Clennell[3] suggest that a blank determination with an amount of aluminium as nearly as possible equal to that in the assay and the same quantities of phosphate and other reagents, should be carried out at the same time as the determination proper. The same writers state that their experiments show that the weight of the ignited precipitate obtained from the same weight of aluminium increases indefinitely as the ratio $P_2O_5 : Al_2O_3$ is increased. This is contrary to the statement of Ibbotson and Aitcheson[21] that the difficulty is overcome by using a large excess of phosphate.

Composition of the Ignited Precipitates.—In order to determine whether or not the low results recorded in Table V were due to the fact that the ignited precipitates did not conform to the formula $AlPO_4$, a number of precipitates were examined and their aluminium and phosphorus contents determined as follows:—The precipitates were dissolved in 10 ml. of conc. hydrochloric acid. The residue of paper-ash, etc., was filtered off and reserved (*a*). To the filtrates 5 g. of tartaric acid were added, and the aluminium was precipitated by the final oxine method which is given in detail on p. 588. The reserved residue (*a*), insoluble in hydrochloric acid, was fused with a little potassium bisulphate, and after extraction with dilute acid the solution was tested for aluminium by the colorimetric method of Lampitt and Sylvester. The filtrates from the aluminium determinations were evaporated with nitric and sulphuric acids to destroy the organic matter, and then 0·5 g. of powdered iron was added and the phosphorus was precipitated with ammonium hydroxide as ferric phosphate. The precipitate was dissolved in nitric acid, and the phosphorus was precipitated first with ammonium nitro-molybdate, and finally with lead acetate as lead "phosphomolybdate" in the usual manner. The addition of iron and subsequent precipitation with ammonium hydroxide is necessary to separate the phosphorus from the sulphuric acid present.

TABLE V

			Weight of $AlPO_4$ precipitates obtained			
			Ignited at 600° C.			
Expt. No.	Aluminium added mg.	Iron added mg.	1st pptn. g.	2nd pptn. g.	Reheated at 1000° C. g.	Aluminium found mg.
14	10·3	nil	0·0426	0·0370	0·0370	8·17
			0·0420	0·0362	0·0363	8·02
15	10·3	nil	0·0435	0·0380	0·0379	8·38
			0·0440	0·0391	0·0391	8·66
16	10·3	2000·0	0·0526	0·0430	0·0432	9·54
			0·0577	0·0416	0·0415	9·17
17	5·15	2000·0	0·0339	0·0147	0·0145	3·20
			0·0286	0·0136	0·0140	3·09
18	10·3	2000·0	0·0683	0·0391	0·0385	8·51
			0·0708	0·0399	0·0396	8·75
19	20·6	2000·0	0·1034	0·0870	0·0870	19·23
			0·1023	0·0862	0·0860	19·03
20	10·3	500·0	0·0586	0·0370	0·0367	8·11
			0·0675	0·0368	0·0366	8·10
21	10·3	500·0	0·0303	0·0044	—	0·98
			0·0478	0·0047	—	1·04
22	5·15	2000·0	0·0313	0·0064	0·0056	1·24
			0·0398	0·0083	0·0078	1·72

The results obtained are given in Table VI, and it will be seen that they are in such close agreement with the theoretical figures that it appears unlikely that any change in the composition takes place under the conditions employed. The precipitates examined were chosen from two batches of samples taken on different days; precipitate A was from a double precipitation from a pure aluminium chloride solution; precipitate B was from a single precipitation from a pure solution.

TABLE VI

Sample	Wt. of $AlPO_4$ ppt. g.	Wt. of residue insol. in HCl g.	Theoretical wt. of Al in ppt. g.	Actual wt. of Al in ppt. g.	Theoretical wt. of P in ppt. g.	Actual wt. of P in ppt. g.
A	0·0379	0·0022	0·0079	0·0077	0·0093	0·0095
B	0·0435	0·0035	0·0088	0·0088	0·0102	0·0098

No aluminium could be detected by the aurintricarboxylate method in the residues insoluble in hydrochloric acid.

Several modifications of the phosphate method were examined; *e.g.* the weak hydrochloric acid solution was boiled, and the aluminium phosphate was precipitated with ammonium acetate instead of sodium thiosulphate; also, ammonium acetate solution was added in the method already studied, after sulphur dioxide had been boiled off,[22] but the results were not materially altered.

Another modification consists in the removal of most of the iron present by means of a sodium bicarbonate separation,[23] followed by a normal phosphate precipitation. This procedure was not studied, since the phosphate method gives low results, whether iron is present or absent.

Recently an attempt was made to apply the phosphate method to the routine analyses of a series of samples of iron containing approximately 7 per cent. of aluminium and 0·75 per cent. of chromium. The chromium was removed from the phosphate precipitate by oxidising it to chromate with potassium permanganate solution and precipitating the aluminium phosphate from the oxidised solution with ammonium acetate solution; the precipitate was dissolved in hydrochloric acid and the aluminium phosphate was precipitated in the usual manner. Check analyses were made on some of the samples by the recommended oxine procedure given on p. 588, chromium being removed before the precipitation of the aluminium, as there described.

It was found that under these conditions the results obtained by the phosphate method were higher than those recorded by the oxine method. This is the exact opposite of the results with chromium-free irons. It was thought that possibly one treatment for the removal of chromium was insufficient, although the phosphate precipitates obtained showed no trace of green colour. Accordingly, a second re-precipitation was made, and when this was done the figures fell below those obtained by the oxine method. The results obtained for a series of these tests in which numerous re-precipitations were made on the same samples are given in Table VII, the last column of which shows the figures obtained for the same samples by the latest hydroxyquinoline method, chromium being removed as described on p. 588.

The figures for the first phosphate precipitation are not given, since some contamination from iron is inevitable at this stage, and thus the figures shown in the first column of Table VII (first re-precipitation) are those which would normally be considered correct.

TABLE VII

Sample No.	First re-pptn.	Second re-pptn.	Third re-pptn.	Fourth re-pptn.	Al (by oxine method) Per Cent.
8784	6·82	6·52	6·20	5·98	6·68
	6·80	6·43	6·24	6·00	6·65
8786	7·54	6·95	6·77	6·23	7·20
	7·55	6·98	6·77	6·25	7·21

The treatment for the removal of chromium was omitted after the second re-precipitation, so that the figures shown in the third and fourth columns of the table were obtained by dissolving the precipitates from the previous treatment in hydrochloric acid and re-precipitating the aluminium phosphate in the usual manner.

It will be noticed from the figures given that the agreement between the duplicates is again excellent, but that the results obtained fall consistently as re-precipitations are made. This fact supports the previous contention that the phosphate method does not precipitate the whole of the aluminium present. It was hoped to obtain a constant figure after the removal of all the chromium present, but, as the results show, this was not so.

The investigation described above has shown that the phosphate method yields low results when applied to chromium-free materials, but that, in the presence of chromium, results obtained by the standard procedure may be high. It was therefore concluded that the phosphate method is unsuitable for the accurate determination of aluminium unless only very small quantities (1 per cent. max.) are present in the samples under examination. The most serious aspect of the matter is that the duplicate tests show excellent agreement, but are, nevertheless, erroneous.

THE HYDROXYQUINOLINE METHOD.—In view of the divergencies reported in the preliminary examination of this method (*supra*) it was decided to endeavour to discover a suitable indicator to enable the precipitations to be made in solutions at a constant *p*H value. The indicators in general use in the laboratory were first tried. To a solution containing 10·3 mg. of aluminium, and free from iron, 5 g. of tartaric acid were added; the volume of the solution was increased to 300 ml., and after the acidity had been adjusted to the change-point of the indicator chosen and the solution warmed to 60° C., precipitation was made with 15 ml. of a 2 per cent. oxine solution followed by 50 ml. of 4 *N* ammonium acetate solution. The beakers and their contents were allowed to stand at 60° C. until the precipitate coagulated and then for a further 45 minutes. The precipitates were collected on a sintered glass crucible (porosity No. 4), washed six times with boiling water, and finally dried to constant weight at 105° to 110° C.

The oxine solution was prepared as recommended by Mitchell and Ward.[24] A 2 per cent. solution of oxine in 2 *N* acetic acid is treated with ammonium hydroxide solution until a permanent white precipitate is produced. The solution is then gently warmed until the precipitate re-dissolves; it is then filtered into the storage bottle and is ready for use. This procedure reduces the amount of free acetic acid present to a minimum.

The results of this stage in the investigation are shown in Table VIII, and it will be seen that none of the indicators employed is really satisfactory. This, however, is not surprising, since both acetic acid and ammonium hydroxide are weak reagents. Methyl red showed the most promise, and was accordingly subjected to further trials, but, after a number of determinations had been made, its use was abandoned, since the results obtained were no better than former figures. The figures obtained are shown in the lower portion of Table VIII.

A search was next made for an indicator with a change-point nearer the neutral *p*H value 7·07, and finally neutral red was chosen for trial.

Neutral Red Indicator.—Neutral red or aminodimethylamino-toluphenazonium chloride has a *p*H range of 6·8 (red) to 8·0 (yellow). It is soluble in water and a 0·5 per cent. aqueous solution was employed. With very weak acid solutions the indicator gives a pink colour, but as the acid concentration increases, the colour changes through red to greenish-purple.

Ammonium acetate solution.—This solution was tested with both methyl red and neutral red indicator solutions. It showed a distinct yellow colour to the former and red to the latter, and thus its *p*H was between 6·4 and 6·8.

Determinations were then made on a series of pure aluminium chloride solutions, and it was found that the neutral red indicator was much more sensitive in hot than in cold solutions. Accordingly, the solutions were first warmed to 60° C., and two drops of the indicator were added; then a 50 per cent. ammonium hydroxide solution was added until the solution was of a distinct yellow colour; this was followed by 10 per cent. acetic acid, added a few drops at a time, until a faint pink colour was produced. The determinations were then completed exactly as in the trials of the other indicators; the results obtained are given in Table IX. It will be seen that they are by far the most satisfactory yet recorded, being both accurate and consistent.

TABLE VIII

Indicator	pH range	Aluminium added mg.	Aluminium found mg.	
Phenolphthalein ..	8·3–10·0	10·3	No reaction in presence of tartaric acid	
Litmus (to first pink) ..	5·0– 8·0	10·3	8·80	8·88
Litmus (to red) ..	5·0– 8·0	10·3	8·69	8·57
Methyl orange	3·0– 5·0	10·3	No pptn. when solution was red	
Methyl red	4·7– 6·4	10·3	9·80	9·81
		5·15	4·22	4·24
		10·3	8·93	9·27
		20·6	19·84	20·50

TABLE IX

Aluminium added mg.	Aluminium found; neutral red used as indicator mg.
10·3	10·17
10·3	10·26
10·3	10·31
10·3	10·30
5·15	5·04
5·15	5·09
5·15	5·10
5·15	5·16
5·15	5·09
5·15	5·10

Several facts, however, were noted during the determinations. Thus, it was found that if, on adding the oxine solution, a precipitate appeared immediately, or at least before all the oxine had been added, the results obtained were of a high standard of accuracy; if, on the other hand, it was necessary to add ammonium acetate solution in order to produce a precipitate, the results tended to be low. By carefully controlling the pH of the solutions, *i.e.* by adding just sufficient 10 per cent. acetic acid to render the solutions pink, but not *red*, immediate precipitations could always be obtained.

In this series of tests some of the precipitates were washed with hot 0·1 per cent. ammonium acetate solution and 0·1 per cent. acetic acid solution instead of hot water, but, as may be seen, no appreciable change in results occurred and the use of hot water was adopted as a standard procedure. It is essential that the washing water should be as near boiling-point as practicable, since 8-hydroxyquinoline is readily soluble in boiling, but practically insoluble in cold water.

Precipitation of Small Amounts of Aluminium.—Attempts were next made to precipitate much smaller amounts of aluminium, and a fresh aluminium chloride solution was prepared by dilution of the original solution; 100 ml. of the aluminium chloride solution (≡ 20·6 mg. Al) were diluted to 1 litre, so that 50 ml. of the new solution were equivalent to 2·06 mg. of aluminium. The determinations were carried out exactly as those just described, neutral red being used as indicator; the results are shown in Table X.

TABLE X

Aluminium added mg.	Amount of 2 per cent. oxine soln. used for pptn. ml.	Aluminium found mg.
2·06	5·0	2·03
2·06	5·0	1·98
1·03	5·0	0·97
1·03	5·0	0·98
0·52	10·0	0·47
0·52	10·0	0·49
0·26	10·0	0·28
0·26	10·0	0·25

It will be seen that they are highly satisfactory for aluminium-contents down to 0·2 per cent. and samples of 1 g. It was, however, noticed that with these small amounts of aluminium, the *p*H of the solution at the time of precipitation was even more important than for higher amounts. Ten per cent. acetic acid must be added until the solution is just tinged pink to the neutral red indicator. If sufficient acetic acid is added to render the solution red, no precipitation of the aluminium takes place, even after the addition of 40 to 50 g. of ammonium acetate. It was also found that better results were obtained by using a comparatively large excess of the reagent, and hence the sudden increase in the amount of oxine solution added for the lower amounts shown in Table X. In all the experiments, except the two lowest recorded (0·26 mg. Al), a precipitate was obtained before the slow addition of the reagent was completed. In the last two experiments it was necessary to add 10 ml. of 4 *N* ammonium acetate solution to produce a precipitate. The precipitates eventually obtained coagulated readily on maintaining the solutions at 60° C. for fifteen minutes, and showed, on filtration and subsequent washing, no tendency to pass through the filters.

THE EFFECTS OF ALLOYING ELEMENTS.—The effects of various elements likely to be present in samples of plain and alloy cast-iron were next investigated, both synthetic solutions and those prepared from actual samples of cast-iron being used.

Titanium.—In all the published literature on the use of hydroxyquinoline in quantitative analysis mention is made of the fact that in acetic acid and acetate solution the element titanium is precipitated. When this statement was checked, however, it could not be substantiated.

The procedure adopted was as follows:—To solutions containing known amounts of aluminium, 5 mg. of titanium were added in the form of the standard solution already described (p. 574), and the determination was completed exactly as before, neutral red indicator being used. The filtrates from the final precipitation of the aluminium as the oxine complex were evaporated with conc. sulphuric and nitric acids in order to destroy the organic matter present, and the titanium was determined colorimetrically. Finally, 10·3 mg. of aluminium were added to a sample of cast iron containing titanium and the separation of the iron was carried out by the hydrogen sulphide and tartrate method, as described earlier, followed by determination of the aluminium exactly as before. The results are shown in Table XI, and from them it is evident that, under the conditions of precipitation established in the course of this work, titanium is not precipitated, and does not, in any way, interfere with the determination of aluminium, since the results recorded for aluminium are not too high and the whole of the titanium added was recovered from the filtrates.

TABLE XI

Expt. No.	Aluminium added mg.	Titanium added mg.	Aluminium found mg.	Titanium found in filtrates mg.
23	10·3	5·0	10·31	5·0
24	10·3	5·0	10·27	5·0
25	10·3	5·0	10·27	4·9
26	10·3	5·0	10·30	5·1
27	5·15	5·0	5·08	4·8
28	5·15	5·0	5·16	4·9
29	10·3	4·6	10·15	—
30	10·3	4·6	10·16	—

In Table XI, Expts. Nos. 29 and 30 represent the sample of cast iron containing titanium, referred to above. It is noteworthy, in view of subsequent results, that these two results for aluminium are slightly lower than others for synthetic solutions recorded in the same table.

Since the vast majority of pig irons contain titanium, the fact that it has been established during this investigation that its presence causes no interference under the conditions described is of considerable importance.

Nickel and Chromium.—In order to study the effects of these two alloying elements, 10·3 mg. of aluminium were added to a sample of cast iron containing 2·52 per cent. nickel and 0·37 per cent. chromium, and the determinations were carried out exactly as before. The precipitate obtained by hydrogen sulphide in ammoniacal tartrate solution was found to contain the whole of the nickel present, as well as the iron and manganese. The precipitate was dissolved in hydrochloric acid and the nickel determined in the usual manner with dimethylglyoxime. The results are shown in the first part of Table XII, and it is evident that the nickel is completely removed by hydrogen sulphide whilst the chromium caused no perceptible interference. It was found, however, that some chromium is precipitated with the aluminium, although, at the relative concentrations of aluminium and chromium used in the previous tests this is insufficient to vitiate the results. The interference becomes more serious as the ratio of chromium to aluminium in the sample approaches 1: 1. If the chromium-content exceeds that of the aluminium the figures recorded for the latter element may be as much as 30 per cent. too high depending upon the actual chromium and aluminium contents of the material.

The results illustrating these facts are shown in the latter part of Table XII, and it will be seen that the amount of chromium precipitated is by no means constant. In all the tests carried out on samples containing chromium considerable difficulty was experienced in preventing its precipitation by ammonium hydroxide with tartaric acid prior to the removal of iron, etc. For samples containing 1·0 per cent. of chromium it was found necessary to double the amount of tartaric acid present. If the chromium-content exceeded 2·0 per cent. it was impossible to prevent its precipitation.

There are two ways in which the interference by chromium can be dealt with. If the chromium-content does not exceed about 1·0 per cent., precipitation may be carried out in the ordinary manner, and the impure aluminium oxine complex dried and weighed, the volumetric method being obviously inapplicable. The precipitate is then dissolved from the crucible in hot hydrochloric acid, the organic matter is destroyed by evaporation with nitric and sulphuric acids, and the chromium is determined by the usual colorimetric method, employing diphenylcarbazide. The chromium figure thus obtained is calculated to its oxine complex, and the weight of the latter is deducted from the original weight of aluminium-chromium complex. In order to make this correction, the composition of the chromium oxine complex was determined. It was found to conform to the formula $Cr (C_9H_6ON)_3$, which contains 10·74 per cent. of chromium.

This method was found to be sufficiently accurate for all practical purposes, but it increases very considerably the time required for the determination. It is far better, therefore, to separate the aluminium and chromium before the hydroxyquinoline precipitation is made. The details of the procedure for this separation are given in the recommended method on pp. 588–589.

TABLE XII

Expt. No.	Aluminium added Per Cent.	Nickel present Per Cent.	Chromium present Per Cent.	Nickel in FeS ppt. Per Cent.	Aluminium found Per Cent.
31	1·03	2·52	0·37	2·50	1·00
32	1·03	2·52	0·37	2·48	1·00
33	1·03	2·52	0·37	2·49	1·05
34	1·03	2·52	0·37	2·48	1·02
35	1·03	2·52	0·37	2·51	1·07
36	1·03	2·52	0·37	2·51	1·01
37	1·50	nil	1·75	—	1·90
38	1·50	nil	1·75	—	1·94
39	1·50	nil	1·75	—	1·63
40	1·50	nil	1·75	—	1·60

In the course of these last experiments it was noticed that on maintaining the solutions and oxine precipitates at 60° C. the solutions acquired a deep red colour and that when this occurred the results were inclined to be high, *e.g.* Expts.

Nos. 33 and 35 in Table XII. For some time no explanation could be found for this phenomenon, since experiments carried out on synthetic solutions containing chromium in various states of valency failed to produce the colour. It was thought that it might be due to some reaction with the neutral red indicator, but in experiments made without the addition of the indicator the colour was still produced.

The trouble was finally found to be due to the presence of traces of bromine, which appear to oxidise the hydroxyquinoline at about 60° C., giving a brown precipitate and producing a deep red colour in the solution. It was concluded that the colour and precipitate were not due to the production of bromine derivatives of the hydroxyquinoline, since the effects could be obtained with other oxidising agents, such as hydrogen peroxide. The action of the latter reagent had already been noticed when making precipitations in ammoniacal hydrogen peroxide solution. Incidentally, this brown precipitate produced by oxidation undoubtedly accounts for the slight dark stain, observed on the sintered glass crucibles after dissolving precipitates in hydrochloric acid for titration, as mentioned on p. 572.

Steps were therefore taken to ensure the complete removal of the bromine used to remove the precipitated sulphur produced after the passage of hydrogen sulphide gas. The slightly modified procedure was as follows:—After the removal of iron, etc., by hydrogen sulphide in ammoniacal tartrate solution, the filtrates were boiled down to a volume of about 100 ml. as previously described. Then 20 ml. of conc. hydrochloric acid were added, followed by sufficient bromine water to colour the solution yellow. Then the solution was boiled down to a volume of 50 ml., by which time the whole of the bromine was expelled.

The method thus modified was employed for all subsequent determinations, and no further trouble was experienced.

Note on the Hydrogen Sulphide Separation.—From time to time during the determinations on samples of cast iron so far described, difficulty was experienced in removing the whole of the iron with hydrogen sulphide. It was found that if the solution was made distinctly ammoniacal prior to the passage of hydrogen sulphide, the iron sulphide precipitate was in a very fine state of division and tended to pass through the filters. If, on the other hand, the solution was made just ammoniacal, the solution became acid before the separation of the iron was complete. Theoretically, from the equation:

$$\begin{array}{llll}
\mathrm{FeCl_2} + \mathrm{H_2S} & \rightarrow \mathrm{FeS} + 2\mathrm{HCl} & & \\
56\text{ g. of Fe} & \rightarrow 73\text{ g.} \quad \mathrm{HCl} & & \\
1\text{ g.} & \rightarrow 1\cdot3\text{ g.} & \equiv 0\cdot605\text{ g. of } \mathrm{NH_4OH} & \\
 & & \equiv 1\cdot85\text{ ml. of } \mathrm{NH_4OH}\text{ (sp.gr. } 0\cdot880). &
\end{array}$$

Hence 1·85 ml. of ammonium hydroxide solution (sp.gr. 0·880) are necessary to neutralise the acid formed when removing 1 g. of iron by means of hydrogen sulphide. Accordingly an excess of 2·5 ml. of ammonium hydroxide was added in every instance and no further trouble was experienced (*cf.* p. 572).

Determinations on Cast Iron.—Since the standard of accuracy attained by the hydroxyquinoline method was now so high, it was decided to apply it to a series of bars containing approximately 7·5 per cent. of aluminium. The determinations were carried out in precisely the same manner as for the synthetic solutions, the hydrogen sulphide and tartrate separation being used prior to precipitation with 2 per cent. oxine solution. The *p*H of each solution was carefully adjusted by means of neutral red indicator solution. Half-gram samples were used instead of the usual 1 g., and these on fractionation, after the sulphide separation, yielded a final sample weight of 0·25 g.

It was first established by experiment that 25 ml. of 2 per cent. oxine solution were sufficient to precipitate 7 per cent. of aluminium when 0·25 gram samples were used.

The results obtained are shown in Table XIII, and it will be seen that they are quite as inconsistent as any recorded for methods without rigid control of the precipitation conditions.

TABLE XIII

Sample No.	Aluminium, per cent.									
	1st Determn.		2nd Determn.		3rd Determn.		4th Determn.		5th Determn.	
7427	6·74	6·94	7·03	7·24	6·44	7·46	7·41	7·57	7·07	7·14
7428	6·61	6·25	6·03	6·21	6·10	6·23	6·51	6·37	6·42	6·26
7429	6·52	6·54	6·76	6·85	6·67	6·59	6·37	6·51	6·70	6·54

Since the modified method had shown such promise when used on synthetic solutions, it was thought that these discrepancies were due to some factor other than the precipitation conditions. Accordingly, a series of cast iron bars containing from 1 per cent. of aluminium upwards was examined with a view to discovering at what percentage of aluminium the method becomes inaccurate. The samples were treated exactly as before, and the results are shown in Table XIV. One-gram samples were employed throughout.

TABLE XIV

Sample No.	Aluminium, per cent.									
	1st Determn.		2nd Determn.		3rd Determn.		4th Determn.		5th Determn.	
7239	1·15	1·14	1·16	1·15	1·14	1·16	1·15	1·16	1·14	1·15
6781	2·24	2·24	2·20	2·19	2·20	2·21	2·19	2·23	2·20	2·23
6758	3·89	3·99	3·92	3·98	3·83	3·97	4·01	3·95	4·02	4·03

It will be seen that the results for samples up to 2 per cent. of aluminium are well within the limits of analytical tolerance, although those recorded for the 2·2 per cent. aluminium sample are not as good as they should be, considering the small amount of aluminium contained by the oxine complex. Above 2 per cent. of aluminium the results become very erratic. A final attempt to overcome these difficulties was made by removing all the silica by baking prior to filtration into a 250-ml. measuring flask. It was realised that this procedure would probably result in slightly low figures, owing to the removal of a little aluminium together with the silica. The residue of graphite, silica, etc., was therefore examined for aluminium by the colorimetric method and all the results are given in Table XV. It will be seen that the removal of silica has no material effect on the results obtained.

TABLE XV

	Aluminium, per cent.				
	Silicon removed		Aluminium in SiO_2 residues	Silicon not removed	
Sample No.					
7239	1·13	1·14	0·01	1·14	1·16
6758	4·01	4·03	0·01	3·83	3·97
6758	4·02	3·95	0·01	3·87	3·79

At this stage of the work the conclusion was reached that the statement of Gadeau,[9] that iron sulphide does not adsorb aluminium, may not hold for amounts of the element in excess of 1 per cent. for 1-gram samples, and a method was therefore sought which would overcome this possible difficulty. The introduction of a re-precipitation of the iron sulphide was deemed impracticable, owing to the difficulty of filtering it off and the ease with which it is oxidised if allowed to stand in contact with air for any length of time.

A review of the other methods available for the separation of iron and aluminium has already been given, and after numerous trials it was decided to employ the sodium bicarbonate separation, followed by a double sodium hydroxide separation.

Sodium Bicarbonate Separation.—In order to carry out this separation, which is described in detail at a later stage, the samples were dissolved in 10 per cent. sulphuric acid, instead of hydrochloric acid, and at first the solutions were evaporated until fumes appeared in order to remove silica, but on 5 g. of sample this procedure led to a loss of about 3 mg. of aluminium, which remained behind with the silica. This necessitated the fusion of the residues with potassium bisulphate, extraction of the melt with water and addition to the main solution. Determinations carried out without the removal of silica showed no appreciable difference in the results, so that this procedure was omitted. No aluminium could be detected in the residues obtained from unevaporated solutions.

When samples containing titanium and vanadium were dissolved in 10 per cent. sulphuric acid, the whole of these two elements was found in the residue of silica, etc., on filtration of the solutions into the 250-ml. measuring flask. For example, in a bar containing 0·15 per cent. of titanium and 0·40 per cent. of vanadium the amounts of the two elements found in the silica residue were 0·14 and 0·38 per cent. respectively. This is a great advantage so far as vanadium is concerned, since, unlike titanium, it is precipitated together with the aluminium under the conditions established in this investigation.

The behaviour of manganese was also investigated, since this element is precipitated by oxine in acetic acid and acetate solution and is incompletely removed by hydrogen sulphide. The greater part of the manganese present is removed by the sodium bicarbonate separation, and examination of the filtrates obtained from this operation on a sample containing 0·73 per cent. of manganese showed that 0·66 and 0·67 per cent. of manganese were present in a duplicate determination. The remainder appears to be removed successfully, together with the iron, since none could be detected in the final aluminium precipitates.

No aluminium could be detected in these bicarbonate filtrates by the colorimetric method, thus showing the completeness of the precipitation of aluminium by sodium bicarbonate.

Between 5 and 10 per cent. of iron remains associated with the aluminium, together with phosphorus and any chromium present. Phosphorus causes no interference, but the iron and chromium must be removed. The removal of chromium is described on p. 588, and for the separation of iron a double sodium hydroxide separation was carried out, but all the results so obtained were high, and precipitates were slightly contaminated with iron. It was found on further tests that it was exceedingly difficult to remove all traces of iron by the sodium hydroxide separation, and after two precipitations by this reagent the solutions contained about 15 to 20 g. of sodium salts, which proved a great disadvantage.

Finally, a return was made to the ammonium sulphide and tartrate separation, which proved highly satisfactory, as subsequent results will show. The procedure, given in detail below, was thus evolved, and extensively tested. It will be noted that the residue obtained by the sodium bicarbonate separation is not ignited and fused, as recommended by many writers. This was deemed unnecessary, since the alternative procedure given proved very satisfactory and no aluminium could be detected in the residue of filter-paper pulp obtained after the treatment of paper and precipitate with hydrochloric acid.

RECOMMENDED 8-HYDROXYQUINOLINE METHOD IN THE ABSENCE OF CHROMIUM.—Dissolve 5 g. of drillings in 100 ml. of 10 per cent. sulphuric acid, filter off graphitic carbon, silica, etc., on a paper-pulp filter, and wash well with hot 5 per cent. sulphuric acid and hot water alternately. Allow the filtrate to cool, dilute to a volume of exactly 250 ml. in a graduated flask, and mix well. For samples containing 1 to 2 per cent. of aluminium, remove 50 ml. of the solution ($\equiv$ 1 g. of the sample) by means of a pipette; (for samples containing 2 to 8 per cent. of aluminium, take 25 ml. $\equiv$ 0·5 g. of the sample) and place it in a 400-ml. beaker. Dilute to approximately 100 ml. with hot water, boil, run in 8 per cent. sodium bicarbonate solution from a burette until a permanent precipitate appears, and then add 4 ml. excess. Boil for one minute and filter rapidly through a 9-cm. Whatman No. 41 filter-paper and wash three times with hot water. The precipitate so obtained will contain all the aluminium present, together with about 5 to 10 per cent. of iron, and usually all the phosphorus.

During this separation care must be taken to avoid excessive oxidation of the ferrous sulphate, to add no more bicarbonate than is necessary, and to filter and wash the precipitate as rapidly as possible. Neglect of these precautions leads to excessive precipitation of iron. For amounts of aluminium in excess of 8 per cent. a larger excess of bicarbonate is necessary; thus for 15 per cent. of aluminium 6 ml. are required.

Transfer the paper and precipitate containing the aluminium, etc., back into the original 400-ml. beaker, add 10 ml. of conc. hydrochloric acid, dilute to 50 ml. with water and boil, stirring continually to break up the filter-paper and prevent bumping. Allow the beaker and its contents to stand on a boiling water-bath for ten minutes and then filter off the paper, washing well with hot water and occasionally putting drops of conc. hydrochloric acid round the edges of the filter.

Dilute the filtrate to about 200 ml., add 5 g. of tartaric acid, and pass a rapid stream of hydrogen sulphide gas for twenty minutes. Filter off any precipitate which may be obtained at this stage and which will contain any copper, molybdenum, etc., present in the iron. After washing thoroughly with 1 per cent. hydrochloric acid saturated with hydrogen sulphide render the filtrate just ammoniacal to litmus and add 2 ml. excess of ammonium hydroxide (sp.gr. 0·800). Pass a rapid stream of hydrogen sulphide through the solution for ten to fifteen minutes; allow the precipitate to settle and filter through a 12·5-cm. Whatman No. 1 filter-paper, washing twice with water containing a little tartaric acid and ammonium hydroxide and saturated with hydrogen sulphide. Dissolve the iron sulphide off the paper into the original beaker with conc. hydrochloric acid and hot water, add 2·5 g. of tartaric acid, make the solution ammoniacal, and pass hydrogen sulphide as before. Filter through a Whatman No. 1 filter-paper, wash three times with the previous washing medium and combine the filtrate with that from the first precipitation of the iron.

Boil the combined filtrates until all the ammonium sulphides are decomposed, and the volume is about 100 ml., and then add 20 ml. of conc. hydrochloric acid. Cool somewhat, add sufficient bromine or bromine water to colour the solution yellow, and boil down to about 50 ml. Filter through a Whatman No. 54 filter-paper into a 400-ml. beaker and wash with hot water. To the filtrate add three drops of a 0·05 per cent. aqueous solution of neutral red indicator, and then add ammonium hydroxide solution from a dropping-bottle until a yellow colour is produced; wash down the sides of the beaker and add 10 per cent. acetic acid, drop by drop, until the solution is just pink. Warm to 70° C. and add, slowly and with constant stirring, 15 ml. of 2 per cent. oxine solution for every 10 mg. of aluminium present, followed by 50 ml. of $4\,N$ ammonium acetate solution. Maintain the solution at 60° to 70° C. until the precipitate coagulates (about 15 minutes), and then filter through a weighed sintered glass crucible (No. 4 porosity) and wash six times with boiling water. Dry the precipitate to constant weight at 105° to 110° C. The precipitate so obtained contains 5.87 per cent. of aluminium.

The need for adhering to the above-described conditions of precipitation cannot be too strongly emphasised, for upon them depends the whole success of the method. The procedure has been applied to a great variety of samples, and some of the results obtained are given in Table XVI. A number of the samples have been previously examined by other oxine methods, and these results will be found in Tables XIII and XIV.

The greater part of Table XVI shows results obtained on a series of samples with an aluminium-content of 1 to 10 per cent. The first sample and the last two have already been included in Tables XIII and XIV. It will be seen that the results are of a high standard of accuracy and consistency. Compared with those previously obtained they are considerably higher except for the 1 per cent. aluminium sample, and therefore support the suggestion that aluminium is adsorbed on the iron sulphide precipitate if more than 1 per cent. of aluminium is present.

RECOMMENDED METHOD IN THE PRESENCE OF CHROMIUM.—Dissolve 5 g. of drillings in 100 ml. of 10 per cent. sulphuric acid and treat the solution exactly as set out in the preceding method until the bicarbonate separation is to be made. Run in 8 per cent. sodium bicarbonate solution from a burette until a slight permanent precipitate appears, and then add 6 ml. in excess. Boil for one minute, filter rapidly through a Whatman No. 41 filter-paper, and wash three times with hot water.

TABLE XVI

Sample No.	Aluminium, per cent.			
	1st Determination		2nd Determination	
7239	1·14	1·15	1·14	1·16
7596	2·37	2·36	2·36	2·36
7597	2·88	2·88	2·86	2·87
7598	3·73	3·74	3·73	3·73
7524	4·23	4·21	4·25	4·23
7525	6·61	6·61	6·63	6·62
6780	7·12	7·13	7·11	7·12
7601	7·47	7·48	7·46	7·47
7527	7·84	7·86	7·85	7·84
7603	9·46	9·46	9·47	9·46
7428	6·64	6·64	6·64	6·65
7429	6·96	6·96	6·97	6·97

Dissolve the precipitate from the filter-paper with 50 ml. of hot 10 per cent. sulphuric acid, dilute to 300 ml. and boil. To the boiling solution add 10 ml. of silver nitrate solution (17 g. per litre) followed by 10 to 15 ml. of freshly-made ammonium persulphate solution (30 g. in 55 ml. of water; saturated solution) and continue boiling for three minutes. Precipitate iron and aluminium by adding excess of ammonium hydroxide and boiling the solution until the issuing vapour no longer smells of ammonia (Lampitt and Sylvester method[14]). Filter off the precipitate on a Whatman No. 54 filter-paper and wash well with hot 1 per cent. ammonium nitrate solution. At this stage the filtrate is generally turbid owing to the silver present. Dissolve the precipitate in hydrochloric acid exactly as described for the bicarbonate precipitate in the previous method, and complete the determination exactly as in the absence of chromium, the silver which has been added to the solution being removed during the passage of hydrogen sulphide through the acid solution.

Application of the above procedure to samples to which known amounts of aluminium and chromium had been added yielded the very satisfactory results given in Table XVII. Experiments Nos. 41 to 43 were on solutions similar to those given in Table XII (Expts. Nos. 37 to 40) and show that the interference due to chromium has been prevented. The aluminium precipitates were tested for chromium by the diphenylcarbazide method, and amounts of the order of 0·00005 g. were found. This shows that the separation of aluminium and chromium described is sufficiently complete for the present purpose.

THE BROMOMETRIC DETERMINATION OF THE ALUMINIUM OXINE COMPLEX.—It has been mentioned previously that the oxine method may be readily adapted for a volumetric finish, and one method of procedure has already been outlined (p. 572). In most of the determinations hitherto recorded the aluminium oxine complex, after being dried to constant weight in order to obtain the gravimetric figures given, was dissolved in hydrochloric acid, and the amount of aluminium present was determined by the volumetric method, but, for the sake of clarity, it was deemed better to deal with this branch of work in a separate section. A few of the results so obtained have already been given in Table II, and it will be seen that they are, generally speaking, unreliable.

TABLE XVII

Expt. No.	Amount of Al added Per Cent.	Amount of Cr added Per Cent.	Amount of Al found Per Cent.
41	1·50	1·75	1·50
42	1·50	1·75	1·51
43	1·50	1·75	1·50
44	1·25	4·00	1·24
45	1·25	4·00	1·23
46	1·25	4·00	1·26

The bromination of 8-hydroxyquinoline has, however, been carefully studied by Fleck, Greenane and Ward,[25] and their work has been substantially verified during the present investigation. It was found that in many instances the end-points of the titrations were variable and indefinite. In all the titrations a certain amount of white solid matter was precipitated, but in many of them a slate-blue solid appeared, which was only slowly decomposed by the sodium thiosulphate solution, and thus caused an unsatisfactory end-point. In the titration of small amounts of 8-hydroxyquinoline, this difficulty rarely occurs, and results are consistent and reliable, but, when dealing with amounts of aluminium above 1 per cent., steps must be taken to avoid the formation of this slate-blue solid. The authors previously mentioned[25] have also observed these facts and suggest the addition of carbon disulphide after bromination as a means of overcoming the difficulty. They further point out that the bromination of hydroxyquinoline by the potassium bromate-bromide solution is not instantaneous, and have experimentally established the fact that from three to five minutes are necessary for this reaction to proceed to completion. The use of carbon disulphide was therefore introduced into the volumetric method under examination, and it was found to be very satisfactory, although, contrary to the statement of Fleck, Greenane and Ward, the slate-blue solid was observed on several isolated occasions when dealing with weights of aluminium oxine complex in excess of 0·6 g. It was further found that chloroform could be substituted for carbon disulphide under certain conditions, but, generally speaking, carbon disulphide is by far the more satisfactory. Carbon tetrachloride is quite ineffective.

The following procedure was therefore devised and extensively used, both on weighed amounts of oxine complex and as a direct volumetric finish to the method already given.

SOLUTIONS REQUIRED: *Potassium Bromate-Bromide.*—For aluminium-contents up to 2 per cent. it is most convenient to use $N/5$ solution, which contains 5·567 g. of pure potassium bromate and 50 g. of potassium bromide per litre. (1 ml. = 0·0004495 g. Al).

For amounts of aluminium in excess of 2 per cent. a solution containing 11·134 g. of potassium bromate and 50 g. of potassium bromide should be used. (1 ml. = 0·0008990 g. Al).

If AnalaR potassium bromate is used and the solution carefully prepared, no standardisation is necessary. If desired, the solution may be standardised by titration against the standard thiosulphate solution.

Sodium thiosulphate.—A solution of the same normality as the potassium bromide is employed, *i.e.* either 50·00 or 100·00 g. of sodium thiosulphate per litre. The stability of this solution will be greatly increased if 0·1 g. of anhydrous sodium carbonate per litre is added. The thiosulphate solution may be standardised, but if the potassium bromate solution is prepared carefully, this is unnecessary.

Indigo carmine indicator.—1·0 per cent. solution in water.

Starch.—A starch indicator which will remain unchanged for several months may be prepared as follows[26]:—Dissolve 1 g. of salicylic acid in 100 ml. of boiling water and add 1 g. of potato starch in a small amount of water. Continue boiling until a clear solution is obtained and then dilute to 1 litre after allowing the solution to cool to room temperature.

PROCEDURE.—The method given on p. 588 is followed in every detail as far as the final filtration of the precipitated aluminium oxine complex. Instead of this being filtered off on a sintered glass crucible, a No. 40 Whatman filter-paper is employed, and the precipitate is washed six times with boiling water; it is then dissolved off the paper with 50 ml. of hot conc. hydrochloric acid (the precipitate is not readily soluble in dilute acid) added in small portions with alternate washings with hot water, into a 500-ml. conical flask. The solution is diluted to 250 ml. with water and cooled to room temperature. (The acid concentration is now 20 per cent.)

Next four drops of indigo carmine solution are added, and the standard potassium bromate-bromide solution is run in, in a thin stream with constant stirring, until the colour of the solution is pure yellow. During this part of the titration the colour of the solution passes from blue to green and finally to yellow. A further two drops of indigo carmine solution are added, and, if the solution shows a green tint, bromate-bromide solution is added until the pure yellow colour is restored. It was found that indigo carmine was a much better indicator than methyl red, since the latter is rapidly decolorised during the titration and continual additions are therefore necessary. When an excess of bromate-bromide solution has been added, the flask is fitted with a rubber bung or glass stopper, well shaken, and allowed to stand for five minutes. Then 10 to 15 ml. of carbon disulphide are added, the mixture is shaken, and 10 ml. of potassium iodide solution are introduced slowly and with constant shaking. Ten ml. of starch solution are added, and the standard solution of sodium thiosulphate is run in until, after vigorous shaking, no trace of blue colour remains in the carbon disulphide layer. At the end of the titration the carbon disulphide is usually pale brown.

With regard to the titration solutions, it should be remembered that the potassium bromate is the true standard, and the sodium thiosulphate solution should be titrated against it exactly as described above, with the addition of indigo carmine, carbon disulphide, etc. In carrying out this titration it is essential to use the same amount (six drops) of indigo carmine solution, as that solution requires about 0·2 ml. of bromate solution to discharge its colour.

CONCLUSION.—This investigation has shown that the 8-hydroxyquinoline method is capable of yielding results of a very high standard of accuracy for a wide range of aluminium-contents, provided that the conditions and modifications given are strictly adhered to. It is applicable to all present-day compositions of alloy cast iron, but when chromium is present special precautions must be taken, especially when the proportions of aluminium and chromium present are of the same order or when chromium is in excess. Normally, chromium is present along with aluminium only in irons intended for very particular applications, although it is likely that, in future, chromium will be added as a special addition to irons containing aluminium. Contrary to published literature, titanium is not precipitated, under the conditions given, by 8-hydroxyquinoline.

The volumetric finish, with its recommended modifications, is quite as accurate as the gravimetric one and greatly reduces the time required for a determination.

After extensive trials it has been shown that the recommended method described is the most accurate yet devised for the determination of aluminium in cast iron and ferrous materials.

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Determination of Nickel and Boric Acid in Nickel-plating Solutions

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THE solution normally used for nickel plating contains nickel sulphate, nickel or sodium chloride and boric acid. For instance, an electrolyte described in a recently-published Air Ministry Process Specification, D.T.D. 905*, has the following composition:—Nickel sulphate, 40 oz.; sodium chloride, 2·5 oz.; boric acid, 5·0 oz.; water, 1 gallon.

A simple and rapid method has been devised for determining nickel and boric acid in such solutions.

The volumetric determination of nickel by means of potassium cyanide usually takes the form of adding the cyanide to a slightly ammoniacal nickel solution containing a suspension of silver iodide, produced by a known amount of silver nitrate, until an excess is shown by the solution becoming clear. The slight excess of cyanide may be found by titrating with silver nitrate.

$$NiSO_4 + 4KCN = K_2[Ni(CN)_4] + K_2SO_4$$
$$AgI + 2KCN = K[Ag(CN)_2] + KI$$

This method gives results close to the theoretical when the concentrations of ammonia and potassium iodide, added to form silver iodide, are kept reasonably small, suitable quantities for a final volume of 50 ml. being five to six drops of conc. ammonia solution and 2 ml. of 2 per cent. potassium iodide solution.

The presence of silver iodide is not essential, though it gives greater precision. If a neutral or slightly ammoniacal nickel solution is titrated with cyanide the precipitated nickel cyanide can itself act as an indicator, the disappearance of the precipitate being taken as the end-point.

Precipitation.—$NiSO_4 + 2KCN = Ni(CN)_2 + K_2SO_4$
Solution.— $Ni(CN)_2 + 2KCN = K_2[Ni(CN)_4]$

The complex nickelocyanide produced is practically neutral, whilst potassium cyanide is very strongly alkaline, permitting of a direct titration to a phenolphthalein end-point, or of the addition of excess of cyanide followed by titration of the excess with acid, methyl orange being used as indicator (Rupp and Pfenning[1]). Obviously the nickel solution must be neutral before titration, and the cyanide must not contain free alkali.

The following experiments were made to test the possibility of proceeding with a titration with sodium hydroxide for boric acid after a titration with potassium cyanide for nickel:

The cyanide solution used was about half-molar and contained only slight amounts of carbonate and hydroxide. Twenty-five ml. of the freshly prepared solution, when treated with excess of mercuric chloride and sodium chloride solution, required less than 0·1 ml. of 0·1 *N* sulphuric acid to give a red colour with methyl red. The end-point with methyl orange was indefinite.

$$2KCN + HgCl_2 = 2KCl + Hg(CN)_2 \text{ (neutral)}$$
$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$$

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* H.M. Stationery Office, price 6d. net.

This solution was standardised volumetrically against silver nitrate and gravimetrically by weighing the silver cyanide precipitated on addition of an excess of silver nitrate. The factor was 0·986.

The nickel solution, made from pure nickel sulphate, and standardised gravimetrically by means of dimethylglyoxime, contained 5·224 g. of nickel per litre, equivalent to approximately 4 oz. of nickel sulphate heptahydrate per gallon; 25 ml. of this solution required for neutrality 0·1 ml. of 0·1 *N* sodium hydroxide, (methyl red as indicator) and 0·15 ml. of 0·1 *N* sulphuric acid (methyl orange as indicator).

Twenty-five ml. of the nickel solution were titrated with the cyanide solution to the complete disappearance of turbidity, several drops of methyl red solution were added, and the alkalinity was determined by titration with sulphuric acid. A check on the result was obtained by then making the solution slightly ammoniacal, adding a little potassium iodide, and titrating with silver nitrate to a slight, but permanent, turbidity.

$$\mathrm{AgNO_3 + 2KCN = KNO_3 + K[Ag(CN)_2]}$$

It appeared interesting to examine the effect produced by small amounts of acid and alkali added before the titration, and Table I gives a comparison between results obtained by titration to the methyl red end-point and those obtained by titration with silver nitrate, after completion of the former titration. In each instance 25 ml. of the nickel solution were used. This volume was equivalent to 18·0 ml. of the cyanide solution, 0·5 *N* × 0·986, as found by titration in the usual manner. The corrected titres in the last two columns are referred to the cyanide solution, and allowance is made for the amount of acid or alkali originally present.

TABLE I

Addition of	KCN required to clear the soln. ml.	Sulphuric acid, 0·1 *N* (methyl red) ml.	Silver nitrate, 0·1 *N* ($\mathrm{NH_4OH}$, KI) ml.	Corrected titres	
				Methyl red	AgI
—	18·05	0·3	0·15	18·0	18·0
—	18·05+0·2 extra	1·0	0·6	18·05	18·0
—	18·05+0·95 extra	5·0	2·5	18·0	18·0
0·1 ml. of 0·1 *N* NaOH	18·05	0·35	0·2	18·0	18·0
1·0 ml. do.	18·1	1·3	0·25	18·05	18·0
2·0 ml. do.	18·05	2·15	0·2	18·0	18·0
1·0 ml. of 0·1 *N* $\mathrm{H_2SO_4}$	18·3	0·35	0·7	18·05	18·0
10·0 ml. do.	20·1	0·3	—	18·0	—

When methyl orange was used instead of methyl red a somewhat vague end-point was obtained.

From these results it can be seen that in a solution, originally neutral, the disappearance of the turbidity produced during the titration occurs at the true end-point, accurate to one drop of 0·5 *N* potassium cyanide. If even small amounts of acid are present in the solution before titration an excess of cyanide has to be added, but, after determining the slight excess alkalinity and allowing for the equivalent in potassium cyanide of the acid originally present, it is found that the quantity of cyanide required for the nickel is unchanged. If small amounts of alkali are present in the solution before titration the end-point with potassium cyanide corresponds approximately with that obtained using a solution originally neutral. A titration with acid then gives a figure for the neutralisation of the alkali added.

Hence, if the original solution is acid, the addition of the correspondingly larger excess of cyanide necessary to clear the solution and to render it slightly alkaline produces free hydrocyanic acid. This acid, although very weak, reacts acid to phenolphthalein, and, in consequence, its presence would interfere with a further titration in the same solution for boric acid. For instance, the hydrocyanic acid produced by neutralising, to methyl red, 5 ml. of the potassium cyanide solution with 0·1 *N* sulphuric acid, required approximately 3 ml. of 0·1 *N* sodium hydroxide to give a red colour with phenolphthalein, in the presence of glycerol.

Table II shows the effect produced by the presence of boric acid on the titration of a neutral solution of nickel by potassium cyanide. The last column gives some figures obtained in titrating the boric acid present. Twenty-five ml. of glycerin were added after neutralising the potassium nickelocyanide solution to methyl red.

It can be seen that boric acid tends to increase the volume of cyanide required to clear the solution, but amounts up to 10 ml. of 0·5 *N* solution mixed with 25 ml. of the nickel solution have only a slight effect.

TABLE II

$NiSO_4$ M × 0·890 ml.	Boric acid 0·5 *N* × 1·008 ml.	Potassium cyanide, 0·5 *N* × 0·986 ml.	Sulphuric acid, 0·1 *N* (methyl red) ml.	Sodium hydroxide, 0·1 *N* (glycerin, phenolphthalein) ml.
—	5·00	—	—	25·2
25·0	—	18·05	0·3	0·3
25·0	5·00	18·05	0·3	25·4
25·0	10·00	18·1	0·6	50·6
25·0	20·00	18·5	2·6	—
25·0	50·0	19·4	6·8	—
5·0	—	3·65	0·3	—
5·0	5·00	3·65	0·3	25·5
5·0	10·0	3·7	0·5	—

The presence of an excessive amount of boric acid, in causing an apparently high cyanide value for nickel, acts like sulphuric acid, but with the former this value may be corrected by titration with sulphuric acid (Table II), if it is known that free alkali has not been introduced with the cyanide solution.

The following method has been found useful in examining nickel-plating solutions.—The solution is diluted ten-fold and 25 ml., neutralised to methyl red, are treated with 0·5 *N* potassium cyanide solution from a burette until the precipitated nickel cyanide just disappears (*a* ml.). The solution is then titrated with 0·1 *N* sulphuric acid (approximately 0·3 ml.), methyl red being used as indicator. Ten to 25 ml. of neutral glycerin are then added, and the solution is titrated with 0·1 *N* sodium hydroxide solution (*b* ml.), phenolphthalein being used as indicator.

1 ml. of 0·5 *N* KCN = 0·007336 g. of Ni
1 ml. of 0·1 *N* NaOH = 0·006192 g. of H_3BO_3

The nickel-content of the original undiluted solution is given by 0·47 (*a* – 0·05), and the boric acid content by 0·40 *b*, expressed as ounces per gallon.

The cyanide solution is standardised most simply by titrating 20 ml. with 0·1 *N* silver nitrate solution.

REFERENCE

1. E. Rupp and F. Pfenning, *Chem.-Ztg.*, 1910, **34**, 321; Abst., ANALYST, 1910, **35**, 220.

166, WICKHAM CHASE
WEST WICKHAM
KENT

February, 1938

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.

MILK FROM MILK BARS

RECENTLY we have had a number of milk samples giving normal values for fat-content, but which were of high specific gravity and gave very high results for non-fatty solids—results higher than any of those we have found hitherto recorded for milks known to be genuine but abnormal. Analyses revealed no colouring matter, no preservatives and no other foreign ingredient. At first it was thought that the samples, though not submitted as such, might have been heated milks whose exceptionally high non-fatty solids were to be accounted for by loss of water through evaporation, or that they might have contained milk reconstituted from milk powder. One sample, it was subsequently found, had been heated; in the other instances the sampling officer was able to say that from his knowledge this was not so. His later investigations showed that the samples were bulk pasteurised milk supplied by large wholesale dairies, and therefore no question need arise that these samples might have been genuine but abnormal milks from individual cows or even a small herd. The milk had subsequently been in cold storage in milk bars, and therefore a possible and reasonable explanation for the abnormalities found is that the milk had frozen and that employees had sold portions before complete thawing had taken place.

Two analyses may be quoted as being typical of the whole series; it will be noted that the Vieth ratio of these was normal:

MILK FROM MILK BARS IN WESTMINSTER

	A	B
Sp.gr. at 60° F.	1037·6	1038·6
Fat	3·90 per cent.	3·51 per cent.
Non-fatty solids	10.20 ,, ,,	10·49 ,, ,,
Ash	0·88 ,, ,,	0·89 ,, ,,
Proteins (by difference) ..	3·82 ,, ,,	3·97 ,, ,,
Lactose	5·50 ,, ,,	5·65 ,, ,,
Vieth's ratio	2·07 : 8·99 : 12·94	2·03 : 9·08 : 12·88

Some time after this work was completed it was brought to our notice that Mr. Stanley Dixon, Public Analyst for Cardiff, had also encountered the same difficulty, and we are indebted to him for giving us permission to include his results in this note. No. 1 was an informal sample taken at a milk bar in Cardiff on April 28th, and No. 2 a formal sample from the same milk bar on May 6th. The second sample was very cold on arrival at the laboratory, and upon enquiry it was ascertained that occasionally ice had been found in the milk, which was kept in a refrigerator from which it was drawn by means of a pump.

MILK FROM MILK BARS IN CARDIFF

	No. 1	No. 2
Sp.gr. at 60° F.	1048·4	1040·5
Fat	3·56 per cent.	3·24 per cent.
Non-fatty solids	12·88 ,, ,,	11·03 ,, ,,
Ash	1·11 ,, ,,	0·93 ,, ,,
Proteins ($N \times 6{\cdot}38$) ..	4·77 ,, ,,	4·12 ,, ,,
Lactose	7·00 ,, ,,	5·98 ,, ,,
Freezing-point (Hortvet) ..	−0·83° C.	−0·688° C.
Vieth's ratio	2·07 : 8·89 : 13·04	2·02 : 8·96 : 13·01

The fact that storage in incorrectly adjusted refrigerators may result in actual freezing should already be well known, but we cannot find that attention has previously been drawn to the consequences of such storage, or that any analyses have been published.

If the assumption implicit in the foregoing explanation be correct, it is obvious that the portions remaining in the receptacles in the milk bars were depleted of some of their non-fatty solids; it is possible that on other occasions this might take place to such an extent as to render the vendors liable to prosecution for deficiency in these constituents. Moreover, although in no instance among the several we have encountered has there been any serious disturbance in the fat-content, it cannot be assumed that this will always be so.

It is no less essential for analysts to be informed of circumstances such as these than for milk vendors to be warned that the obvious remedy is to control the temperature of cold storage more carefully. A disregard of this simple precaution amounts to improper handling, just as does lack of adequate stirring, and it cannot possibly be argued that a defence based on the effect of refrigeration will avail in a court of law.

Since this note was first submitted for publication we have seen the report of a case (*British Food J.*, June, 1938, p. 59) regarding the sale of milk containing extraneous water. The defence put forward was that the extraneous water was due to refrigeration, but this was not accepted and the magistrate imposed a fine on the defendants.

Another case relating to deficiency in fat in milk sold at a milk bar at Chester is also recorded in the same journal. (*Cf.* also p. 602 of this volume.)

F. W. EDWARDS
H. R. NANJI

ANALYTICAL LABORATORIES
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THE DIRECT DETERMINATION OF AMMONIA IN WATER

THE direct method for determining ammonia in water described by Kitts (ANALYST, 1938, 172) has been applied to a number of waters, with very satisfactory results. One sample known to have a fairly high free and albuminoid ammonia content proved an exception. This water after treatment with acid and persulphate gave not the slightest colour with Nessler's reagent. Further examination showed that the water contained 23 parts of chlorine per 100,000.

Salt solution was treated with persulphate and acid, and on addition of *o*-tolidine reagent the presence of free chlorine was demonstrated. It is known that chlorine and ammonia react in acid solution to form nitrogen chloride which is unstable; on warming, nitrogen gas is evolved. This accounts for the loss of ammonia from the water under consideration. Experiments were made to determine the concentration at which chloride would interfere with the test. Up to 5 parts of chlorine per 100,000, no loss of ammonia was observed; over this amount the error increased and the presence of 18 parts caused complete loss of ammonia. This particular water, when diluted tenfold with ammonia-free water (thus reducing the chlorine to 2·3 parts per 100,000) gave figures for albuminoid ammonia identical with those obtained by distillation.

Other waters have been observed to darken when treated with persulphate and acid. This darkening, which is due to the presence of manganese, fades very slowly in the cold with the Rochelle salt solution. If the Rochelle salt is added to the hot solution the discoloration quickly disappears, but leads to a serious error due to oxidation of the tartrate to an aldehyde which gives a colour with Nessler's reagent very similar in appearance to that given by ammonia. Such waters are best dealt with by adding a crystal of oxalic acid to the warm solution after treatment with persulphate, and some Rochelle salt just before Nesslerising.

J. C. HARRAL

CITY AND COUNTY ANALYST'S OFFICE
BRADFORD, YORKSHIRE

Notes from the Reports of Public Analysts

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

CITY AND COUNTY OF BRISTOL

REPORT OF THE PUBLIC ANALYST FOR 1937

OF the 1898 samples examined under the Food and Drugs Act, 630 were taken formally.

ICE CREAM.—Three of 9 samples examined contained only a negligible amount of fat (0·12, 0·13 and 0·15 per cent.) and were condemned. The percentages of fat in 90 samples examined during the past eight years ranged from 1·5 to 14·7 per cent. As the word "cream" seems particularly inappropriate to samples containing not more than 0·15 per cent. of fat, it was decided by the Health Committee to bring the matter before the Ministry of Health, enclosing the certificate of analysis, and to suggest that some action should be taken.

SAUSAGES "CONTAINING NO BREAD."—Two samples of beef sausages, sold to the inspector as "containing no bread," were found to consist of approximately 35 per cent. of meat and 65 per cent. of fillers, water and a fluorescent dye. Microscopically the starch present was indistinguishable from that of rusk or biscuit-meal. Both samples were condemned, but, owing to the warranty held by the defendant, the case was withdrawn. F. E. NEEDS

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1937

"TEA AND COFFEE CREAM."—Three samples, sold as "Tea and Coffee Cream," "Tea Cream" and "Fruit Cream," contained respectively 21, 26 and 25 per cent. of butter-fat. The sale of cream with such low fat-content appears to be a direct result of the suggestion in the Report of the Reorganisation Commission for Milk that its sale for use with breakfast cereals, etc., should be encouraged. Its cheapness, as compared with rich cream, would be an added inducement to its purchase, and, at the same time, it would offer competition to foreign tinned cream, which usually contains 20 to 25 per cent. of butter-fat. On the other hand, there may be a great temptation to sell the article of lower quality at the price of genuine rich cream—a state of affairs which would not arise if a declaration of the content of butter-fat were required by law.

STAINLESS IODINE OINTMENT.—Ten samples examined contained from 1·3 to 5·0 per cent. of iodine. The directions for making non-staining iodine ointment given in the B.P. Codex and in the National Formulary for National Health Insurance require the addition of 5 per cent. of iodine, but give no indication as to the amount of iodine that should be present in the finished ointment. From the examination of ointments prepared by several well-known manufacturers the conclusion was arrived at that with care 4·5 per cent. of iodine could be retained, and that in any event not less than 4·0 per cent. should be left. One sample, which contained 3·3 per cent. of iodine, was packed in glass jars with screw-on tinned iron covers, and the metal of the cover had been extremely corroded by the iodine. The manufacturers' attention was called to the unsatisfactory condition of this preparation, and they were asked to withdraw from sale all the stocks in the City. There were no mitigating circumstances in connection with a sample containing 1·8 per cent. of iodine, and proceedings were instituted; the retailer was fined 5s., and the manufacturers, for aiding and abetting the offence, were fined £5 and £3 3s. costs.

DISINFECTION OF CLOTH CONTAINING ALUM AND MAGNESIUM SULPHATE.—A piece of cloth cut from bed ticks which had been treated in the Corporation disinfector was found to have developed holes merely on handling. The cloth was found to have been "filled" with a mixture of alum and magnesium sulphate, and, although under the ordinary conditions of use these salts have no deleterious effect, when such fabrics are submitted to dry heat, as happens in a disinfector of this type, in which super-heated steam followed by dry air is used, it is well known that magnesium sulphate has a tendering action on the fibres, while the action of alum is very much greater and will quickly rot them. G. H. WALKER

Annual Report on Alkali, &c., Works for 1937*

THE seventy-fourth Report of the Chief Inspectors to the Ministry of Health and to the Department of Health for Scotland gives the usual survey of the work done in carrying out the provisions of the Alkali, &c., Works Regulation Act, 1906, and in connection with the work of smoke abatement.

The number of works registered in 1937 was 980, involving the operation of 1835 separate processes. The totals, compared with those of last year, show an increase of two works and a decrease of 15 processes. As in previous years, sulphuric acid, chemical manure, sulphate of ammonia and tar plants show a decrease, whilst the number of muriatic acid, gas liquor and benzene plants is increased. The reduction in the number of plants does not necessarily mean a

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1s. net.

lower production; on the contrary, centralisation more usually results in higher production.

In connection with the inspections 2357 quantitative analyses of the chimney and other gases escaping into the atmosphere were made. The results, expressed as grains per cubic foot, are summarised in the following table:—

	General average		
	1937	1936	1935
1. *Hydrochloric Acid.*			
(*a*) from alkali and wet copper works	0·077	0·079	0·075
(*b*) from tinplate flux works	0·075	0·078	0·078
(*c*) from salt works	0·054	0·067	0·058
2. *Total Acidities* (in terms of SO_3):—			
(*a*) from sulphuric acid works	1·54	1·62	1·61
(*b*) from oleum works	3·39	3·34	3·99
(*c*) from sulphuric acid concentration works ..	0·70	0·63	0·50
(*d*) from Venetian red works	1·05	0·82	0·92
(*e*) from smelting works	2·58	2·35	2·35
(*f*) from chemical manure works	0·06	0·08	0·06
(*g*) from other registered works	0·68	0·66	0·66
3. *Total Acidities* (in terms of SO_3):—			
(*a*) from all registered works	1·06	1·03	1·07
(*b*) from all registered works except smelting works	0·87	0·86	0·90

A particularly pleasing feature of the year has been a revival of trade in South Wales. Increased demands for coal and steel, the development of an extensive trading estate and afforestation schemes have given renewed hope and encouragement and there is apparent in the district a greater feeling of optimism and vitality. An outstanding feature has been the development of a large new strip mill combined with a tinning plant and coke ovens at Ebbw Vale.

SMOKE ABATEMENT.—The Alkali Inspector has no statutory powers in this connection, his function being purely an advisory one. Powers of compulsion and prosecution are vested in the Local Authorities. Inspectors have kept in touch with Regional Committees and have attended meetings of the Liverpool, Manchester and West Riding Committees. It is regretted that no definite move has been made towards the establishment of new Regional Committees, though it is likely that one will be set up to represent London, and it is possible that one will also be formed in the Bristol district.

The Potteries constitute a fairly big region where this problem is essentially a common one and smoke emission is conspicuously high. It is therefore a particularly appropriate district for the formation of an active Regional Committee, and it is a matter of great disappointment that one of the authorities has not yet seen its way to take this view.

Most of the complaints which have been brought to the notice of the department have related to grit emission from boiler installations, coal and coke grading plants, and from the handling of pulverised fuel. There has been much outcry, for instance, relating to the emission of grits from a pulverised fuel fired plant in Wales.

POWER STATIONS.—The washing plant at the Battersea Power Station has continued in satisfactory operation. The average of official tests made for determination of total acidity was 0·023 grain (expressed as S) per cb. ft. of dry gas at N.T.P. This average is corrected to a basis of 10 per cent. CO_2 in the chimney gas.

The following figures, which are supplied by the London Power Company, relate to the operation of their gas-washing plant in 1937:

Total weight of coal fired	480,133 tons
Average sulphur content of coal	0·86 per cent.
Total volume of gas treated	$1{\cdot}9 \times 10^{11}$ cb. ft. (dry at N.T.P.).
Average CO_2 content of gas	12·4 per cent.
Average total acidity of the emissions (879 works tests)	0·032 grain (as S) per cb. ft. of dry gas at N.T.P.
Equivalent of sulphur eliminated by gas washing	3,734 tons.

The gas-washing plant at Fulham has operated with even more remarkable efficiency.

Carbon Disulphide Works.—Although conditions of manufacture at this class of work have been improved, there are still occasions when fumes are noticeable. The charging and scurfing of retorts are operations which are doubtless partly responsible, and special attention has been directed to them. In one works new and larger Claus kilns have been put into operation for dealing with the residual gases from the carbon disulphide process, and sulphur of good quality is recovered. It was thought at one time that, by sufficient preheating of the charcoal, it would be possible to avoid altogether the formation of hydrogen sulphide, but in practice it has been found that, although the amount can be greatly reduced, the production cannot be totally inhibited, and it is therefore necessary that the tail gases, after removal of carbon disulphide, should be properly treated.

The recovery of carbon disulphide is now practised at six factories in England, and at one in Scotland; the solvent is adsorbed on active carbon and recovery is effected by steaming. Efficiency of adsorption averages about 96 per cent. (sometimes higher), but after taking into account losses due to handling, etc., the net recovery based on solvent purchased is about 75 per cent.

Treatment of Offal.—Considerable attention has been given during recent years to the statutory offensive trades under Section 32 of the Public Health (Scotland) Act, 1897.

The process of offal treatment is essentially one of desiccation, whether carried out in a batch of concentraters, or digesters, or in continuous dryers. The vapours from the machines are in the first place passed through contact condensers in order to condense the water vapour and to remove the soluble constituents of the gases. Suction is provided by means of fans placed after the condensers and the foul gases are deodorised by (*a*) treatment with gaseous chlorine, (*b*) scrubbing with hypochlorite solution, or (*c*) incineration.

Oxidation of the objectionable constituents of the foul gases by means of gaseous chlorine is receiving increasing attention and, where it has so far been adopted, has proved eminently satisfactory from the point of view both of the manufacturer and of the sanitary authorities. In the latest method, chlorine is supplied in cylinders and is injected into the foul gas stream at a point immediately on the suction side of the fans, after the water vapour content of the gases has been removed in the condensers. The rate of chlorine flow is controlled by an automatic administrator and the amount arranged according to the input of raw material; the quantity of chlorine required for complete deodorisation has been determined at 0·9 lb. per ton of fresh fish or flesh offal.

New Zealand

ANNUAL REPORT OF THE DOMINION LABORATORY FOR 1937

THE Acting Dominion Analyst (Mr. R. L. Andrew, F.I.C.) reports that the total number of samples examined for various Government Departments in the main Laboratory and the three branches was 12,132, of which 9675 were for the Health Department.

SALE OF REFRIGERATED MILK.—An interesting case of low solids and freezing-point indicating added water was investigated; the milk in a retail dairy had been kept in a cabinet below freezing-point, so that the first customers obtained the milk concentrated by freezing and the later customers the diluted milk. The firm was prosecuted to draw attention to this form of unintentional adulteration. (See also Edwards and Nanji, p. 596.)

OFFICIAL REDUCTASE TEST.—A comparison of the New Zealand official reductase test with the English method of inverting the tube every half hour has been carried out during the year, and has indicated that it will probably be desirable to adopt the English modification.

The legal minimum requirement for the reductase test is that the milk shall not decolorise the methylene blue in less than three hours, but the percentage of samples causing reduction in five hours or under was only 3·4. This indicates that the legal minimum could with advantage be increased to five hours.

BRANDS OF ASPIRIN.—All the available brands of acetylsalicylic acid (aspirin) sold in tablet form were examined, with most interesting results. It was found that without exception they complied with the standard of the British Pharmacopoeia, and for practical purposes were all equally pure and of high quality. In some instances the statements in the accompanying literature would by inference be misleading, such as a warning against purchasing impure aspirin when all the brands sold are of equal purity. One brand was described as more effective than aspirin, but aspirin is simply a synonym for acetylsalicylic acid, and the tablets were sold as such. Several makes were advertised as "Does not affect the heart." The samples being all of the same degree of purity, this statement if correct would apply equally to the other brands. The different brands varied widely in price although practically identical in quality, and afford an interesting illustration of the effect of advertising.

ARSENIC ON SPRAYED CABBAGES.—In an investigation of the amount of spray residue on cauliflowers and cabbages the cauliflowers were sprayed with arsenate only before the flower had formed, and as a rule no residual arsenic was detected. The maximum amount of arsenious oxide found was $\frac{1}{7000}$ grain per pound.

The results on the cabbages showed that, of 100 samples, in only two instances, did the residual arsenic in the heart of the cabbage exceed $\frac{1}{100}$ grain of arsenious oxide per pound, but that with the whole cabbage, when only a short period had elapsed between the final spraying and harvesting, the residue might be as high as $\frac{1}{10}$ grain of arsenious oxide per pound.

DECIPHERING NUMBERS FILED OFF METAL.—Numbers which had been filed off several stolen bicycles were made visible by using a solution of copper chloride in hydrochloric acid containing 5 per cent. of glycerin, the solution being kept saturated by means of a freezing mixture until application. A small reservoir of dental sheet was made round the number and the solution was applied several times for short periods.

Hong Kong

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

In his Annual Report the Government Analyst (Mr. V. C. Branson, F.I.C.) states that the year 1936 was a record one as regards the amount of work done by the Government Laboratory. The number of samples examined (4339) was 10 per cent. higher than for 1935.

COUNTERFEIT COINS.—At the beginning of the year there was a large influx of counterfeit coins purporting to be the new (1935) mixed metal 10 cent pieces. Most of these coins were made of an alloy of the german silver type although one batch had practically the same composition as a genuine one. These coins were "struck" coins not moulded and there were minor errors in design. In view of the huge amount of work involved in analysing these coins—batches were being brought in several times a week—and also as they could be detected as counterfeit by visual examination, it was decided that, in cases involving only possession, these coins should not be brought for analysis. In one case actual dies and presses for making coins were discovered; these were counterfeit of Queen Victoria 5 cent pieces and were of copper, silver-plated. They were exceedingly good copies and the die was very carefully made.

FOOD AND DRUGS ORDINANCE.—On July 1st the long-awaited Adulterated Food and Drugs Ordinance came into force. Of the 196 samples examined, 150 were genuine, the adulterated articles including 19 of vinegar (all the samples), 7 of milk, 9 of mustard and 5 of tea.

The adulterated teas all consisted of old used leaves, some of which had been collected from spittoons, etc., dried and sold again.

The vinegars were all locally made and, as a result of investigation, it was decided to lower the standard of 4 g. of acetic acid per 100 c.c.

TOXICOLOGICAL CASES.—Of the 199 specimens examined, no poison was found in 66 cases. For suicidal purposes, opium (42 cases), and poisons of the lysol type (17 cases), were still the favourite agents, but there was an increase in the number of cases involving the use of barbituric acid derivatives.

Gelsemium Poisoning.—Gelsemium elegans Benth., a native poisonous herb, caused death on three occasions. In each case the herb was apparently taken in mistake for a non-poisonous Chinese herb.* Potassium permanganate was used on three occasions for suicidal purposes, and in the one fatal case the deceased had swallowed the substance in solid form. There was another unusual case in which water-glass (sodium silicate) had been swallowed, with fatal results.

Fish poisoning.—Two cases of fish poisoning occurred in which several people lost their lives through eating a Chinese fish known as Kai Po Yu. This fish is poisonous if cooked in certain ways, but the actual poison gives no recognisable chemical reactions.

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* The medicinal plant is the Carolina jasmine, *Gelsemium sempervirens*.—EDITOR.

British Standards Institution

THE following Standard Specification has been issued*:

* Copies may be obtained from the Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. net; post free 2s. 2d.

NO. 795—1938. AMPOULES.

The specification is divided into five parts as follows:—Part (1) Flat-bottom straight neck ampoules. Part (2) Round-bottom tapered neck ampoules. Part (3) Flat-bottom constricted neck ampoules. Part (4) Flat-bottom drawn-out neck ampoules. Part (5) Flat-bottom sloping-shoulder, open-ended ampoules.

Each section gives the range of sizes, capacity of the bulb, dimensions and material from which the ampoule is to be made, the inscriptions to be marked on the ampoule, and the particulars in regard to the base and neck. There is also an Appendix giving the test for the limit of the alkalinity of the glass.

DRAFTS OF SPECIFICATIONS IN COURSE OF PREPARATION

A limited number of copies of the following Draft Specifications are available, for the purpose of technical comment, to specially interested members of this Society, who should apply directly (mentioning their membership of this Society), and send their comments directly, to the British Standards Institution, 28, Victoria Street, London, S.W.1:

C/11/9. DRAFT STANDARDS FOR CHEESECLOTH AND BUTTER MUSLIN.
C/11/4. BRITISH STANDARD METHODS FOR THE MICROBIOLOGICAL EXAMINATION OF BUTTER.
C/45/2/6. REVISED DRAFT BRITISH STANDARD METHOD FOR THE DETERMINATION OF THE FUSION TEMPERATURE OF COAL ASH (B.S. 453).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Mutarotation of Honey. S. Mihaéloff. (*Ann. Chim. anal.*, 1938, **20**, 145–149.)—An investigation of the various methods suggested for destroying mutarotation led to the following conclusions:—The choice of clarifier is important: aluminium hydroxide and kieselguhr are sometimes inadequate and tend to produce slightly turbid solutions. Lead acetate (the excess being removed by sodium phosphate) is more rapid and precise in its action. Simple boiling for 5 minutes does not abolish mutarotation even in three hours after cooling. The action of alkali (ammonia or sodium carbonate) is, as a rule, more rapid than boiling but, with some samples, it was necessary to wait for three hours. Allowing the solution to stand for 24 hours appears to be the most certain method of obtaining constant results. Certain honeys, especially the brown dextrorotatory pine honeys continued to change even after several days, the change being unaffected by clarification with kieselguhr or aluminium hydroxide, whilst lead acetate arrested its development. This change may be due to the slow hydrolysis of dextrins, and with these honeys the amount of reducing substances present increased day by day with the diminution of optical rotation. The method finally recommended is to allow the solution to stand for 24 hours after clarification with lead acetate and to remove the excess of lead salt with sodium phosphate. With dextrorotatory honeys a second solution clarified with kieselguhr or aluminium hydroxide should be used to follow the progress of mutarotation. A. O. J.

Determination of Copper and Iron in Some Argentine Musts and Wines. L. de Prado. (*Ind. y Quimica*, 1937, **2**, 67–71.)—Twenty ml. of the wine were treated with 1 ml. of sulphuric acid (1 in 3) and 5 ml. of nitric acid, the mixture was evaporated on the water-bath, and the residue was calcined to eliminate the sulphuric acid. The crucible was cooled in the oven, the residue was dissolved in water, and the solution was treated with 3 drops of nitric acid in 20 per cent. hydrochloric acid. The liquid was evaporated on the water-bath and the residue was taken up in water and made up to 25 ml. Ten ml. were taken for the colorimetric determination of copper by a modification of the diethyldithiocarbamate method, and 10 ml. for the colorimetric determination of iron as thiocyanate. The wines analysed contained 0·25 to 2 mg. of copper per litre (average 1·05 mg.). There was no pronounced difference in copper-content or in sulphate-content between wines from different regions. Musts are rich in copper, an average value of 22·9 mg. per litre having been found in musts from grapes, some of which had been treated with copper sulphate. The same grapes, washed, gave 0·8 to 1·8 mg. per litre, and wines made from these musts contained, on the average, 3·5 mg. per litre. Some copper is lost by precipitation during fermentation. Twenty-one samples of wine gave an average iron-content of 25 mg. per litre, and 10 samples of musts gave 24·4 mg. per litre; the wines from these musts contained, on the average, 10·5 mg. of iron per litre, iron being lost by precipitation during fermentation. E. M. P.

Composition of the Seeds of *Cajanus* Sp. and *Canavalia* Sp., Brazilian Native Foods. F. W. Freise. (*Z. Unters. Lebensm.*, 1938, **75**, 566–568.)—These leguminous plants (sub-order *Papilionaceae*) are frequently known as guandú (more rarely andú) and feijao d'Angola (Angola bean) respectively, and are cultivated in most regions of Brazil as food for human beings and cattle, while their by-products are used for various domestic purposes. *Cajanus seeds.*—The wrinkled pods contain from four to nine almost spherical seeds, 4 to 5·8 mm. in diameter. They vary in colour and a single pod may contain yellow, green, grey, brown and black seeds with or without surface markings. The shell amounts to 2·0 to 2·35 per cent. of the total weight of the cultivated seed and in seeds from wild plants may reach 4 per cent. The following results (per cent.) were found for unshelled, air-dried seeds, the range given indicating the variation due to differences in the age of the plants (1 year and 6 years) and differences in the two types of soil (weathered granite and sandy), and the other figure being the corresponding figure for a plant grown from wild seed. Water, 12·8 to 15·5, 16·4; nitrogenous matter, 23·6 to 24·65, 25·16; fat, 1·70 to 2·05, 2·22; carbohydrates, 52·11 to 55·15, 48·96; cellulose, 2·25 to 3·15, 3·82; ash, 3·29 to 3·80, 3·60. The shell contains small amounts of a rather strongly diuretic essential oil having the odour of fresh butter and a slightly burning taste. It gave the following constants:—sp.gr. (20°/4° C.), 0·925; optical rotation,—0° 50′; n_D^{20} 1·4845; b.p. (760 mm.), 193° C.; acid value, 4·6 to 6·4; ester value 45 to 53; heat of combustion, 2494 to 2529 cals. *Canavalia seeds.*—Twelve species of this genus are used in Brazil for such purposes as tanning, fibre making and basket weaving. The species cultivated for food are *C. ensiformis* D.C., *C. albiflora* Ducke, *C. gladiata* (L.) D.C., *C. dictyota* Piper

(= *C. gladiata* var. Benth.), *C. amazonica* Piper and, in emergency, during periods of drought, *C. obtusifolia* D.C. The following average figures (per cent.) were obtained from a large number of samples of canavalia seeds, the deviation from the mean being from 2 to 3 per cent. Water, 13·78; nitrogenous matter, 23·45; fibre, 8·58; starch, 44·84; total sugars (as sucrose), 2·23; fat, 3·54; ash, 3·58. *C. obtusifolia* is slightly toxic owing to the presence of cyanogenetic glucosides, 0·0125 to 0·0185 per cent. of hydrocyanic acid being obtainable from fresh seeds. Only the radicle and silver skin contain hydrocyanic acid, the cotyledons being free. Fresh pods contain up to 0·021 per cent. of hydrocyanic acid, which disappears as the beans dry and harden. If the seeds are boiled before being used as food there is little danger; a more harmful practice is their use as diluents of tapioca meal in the preparation of bread substitutes. The ash contains up to 32 per cent. of potassium oxide, 0·6 to 0·8 per cent. of sodium chloride and up to 6·85 per cent. of phosphoric acid. Canavalia seeds are sometimes used in the preparation of infant foods and similar products. A. O. J.

Examination of "Brick Tea." L. Schuler. (*Z. Unters. Lebensm.*, 1938, **75**, 572–574.)—This product, which is compressed into blocks, is little used in Europe. Its bad reputation, due to some samples containing inferior grades of tea, is not always deserved. The material examined was of Manchurian origin and was apparently intended for sale among the Russian inhabitants of that locality. Its composition was as follows:—Water (loss at 105° C.), 9·89; caffeine (on dry sample), 2·19; ash, 7·38 (of which 2·75 per cent. was soluble in water, 2·27 per cent. was sand and the remaining 2·36 per cent. consisted of acid-soluble oxides and silicates); essential oil, 0·09; water extract, 32·9; tannin, 8·47; crude fibre, 16·48; fat (wax), 0·69 per cent. A microscopical examination indicated that the substance consisted of normal tea with the inclusion of a certain amount of the young leaves. A. O. J.

Source of the Condiment "Spanish Hops." C. Griebel. (*Z. Unters. Lebensm.*, 1938, **75**, 568–572.)—A sample of mixed spices was found to contain "Spanish hops," a herb which resembles marjoram, and is used as a source of essential oil and, occasionally, as a spice, especially in the pickling of anchovies. This spice is generally referred to the source *Origanum creticum* L., and the herb occurs in commerce under the name *Herba origani cretici*. Recently, *Origanum creticum* has been considered as a related form of *Origanum vulgare* L., subsp. *prismaticum* Gaud. The portions of leaf picked out from the mixture were dotted with yellowish or reddish oil-glands and, when they were rubbed between the fingers, an odour resembling that of marjoram or coriander was apparent. The leaflets were sparsely haired, the pubescence being denser at the margin and along the veins of the lower surface; it was less dense than that of marjoram. The very rigid, two- to five-celled articulate hairs have thick cell walls, and a unicellular tooth-like or dagger-shaped hair with a very thick wall occurs occasionally at the margin. The distribution of oil glands on the surface appears closer than in marjoram. Marjoram is placed by some authors in the genus *Origanum* (*Origanum majorana* L.), others divide the genus and name marjoram, *Majorana hortensis* Mönch. The principal difference between *Origanum* and *Majorana*, considered as separate genera, is in the form of the calyx, which, in *Origanum*, is bell-shaped and five-toothed, whilst in *Majorana* the sepals are fused into a single leaf-like structure. Examination of commercial specimens of *Herba origani cretici* indicated that some consisted of *Origanum* spp. and others of *Majorana* spp. This lack of homogeneity in commercial samples was noted by Hartwich (*Real-Enzyklopädie der gesamten Pharmazie,* 1889, **7**, 558). In order to compare the herb in question with those from a number of possible sources, two samples of *Majorana onites* Benth., six specimens of *Origanum vulgare* L., var. *creticum* Briqu., five specimens of *Origanum hirtum* Vog. and one of *Origanum smyrnaeum* L. were procured. There was considerable variation among these specimens in hairiness, distribution of oil glands and formation of the calyx and, of the six specimens of *Origanum vulgare,* only two agreed among themselves. It appeared probable that the spice herb belongs, not to *Origanum vulgare* L., var. *creticum* Briqu. but to *Origanum hirtum* Vog. The five specimens of this herb differed in hairiness, etc., but agreed among themselves and with the spice herb in the distribution and colour of the oil glands. According to Hegi, *Origanum hirtum* Vog. is distinguished from *O. vulgare* by the denser distribution of oil glands on the calyx. *Majorana onites* Benth. has a rather dense distribution of oil glands on the leaves, which are densely pubescent, especially on the prominent veins of the lower surface. The articulate hairs have two or three cells (more rarely up to six) the walls of which are sometimes strongly thickened. As in *O. hirtum,* these hairs are often broken off at the tip of the basal cell, and the hair then may be mistaken for a unicellular peg-shaped hair. Occasionally dagger-shaped unicellular hairs with very narrow lumina are found on the margin. Many of the hairs contain minute rod-shaped crystals. It thus appeared that the herb known in commerce as *Herba origani cretici* or "Spanish hops" or sometimes merely "hops" is derived, not from *Origanum vulgare* L., var. *creticum* Briqu. (*O. creticum* L.) but partly from *Origanum hirtum* Vog. and partly from *Majorana onites* Benth. A. O. J.

Biochemical

Photoelectric Method for the Micro-Determination of Sodium in Serum and Urine by the Uranyl Zinc Acetate Precipitation. W. S. Hoffmann and B. Osgood. (*J. Biol. Chem.,* 1938, **124**, 347–357.)—To 0·2 ml. of serum in a 15 ml. conical Pyrex centrifuge tube are added 0·2 ml. of 6 *N* sulphuric acid and 0·1 ml. of conc. nitric acid. The tube is placed in a boiling water-bath for 10 minutes to hydrolyse the protein and is then heated carefully over a free flame until charring has occurred. The charred material is allowed to cool for 30 seconds, a drop of 30 per cent. hydrogen peroxide is then added, and the heating is resumed. The addition of the hydrogen peroxide is repeated until only a colourless drop of sulphuric acid digest remains; 6 drops are usually required. To the cooled solution so obtained are added 8 ml. of uranyl zinc acetate solution. [This is prepared by heating 80 g. of uranyl acetate and 48 g. of 30 per cent. acetic acid with 392 ml. of water until solution is complete; 220 g. of zinc acetate and 24 g. of 30 per cent. acetic acid are dissolved in 276 ml. of water. The two solutions are mixed and the mixture is cooled and saturated by adding 0·2 g. of "triple salt" (uranyl zinc sodium acetate); portions of the solution are filtered before use. The "triple salt" is prepared by adding 125 ml. of the uranyl zinc acetate solution to 5 ml. of 2 per cent. sodium chloride solution and filtering after allowing the solution to stand for 15 minutes. The precipitate is washed 5 times with glacial acetic acid and 5 times with ether and dried in a desiccator.] The mixture is stirred for 2 minutes with a small rod which is then washed with a little uranyl zinc acetate solution and removed. After 15 minutes, the tube is centrifuged, and the supernatant liquid is discarded. The precipitate of "triple salt" $(UO_2)_3ZnNa(CH_3COO)_9{\cdot}6H_2O$ is washed with 2 ml. of acetic acid and alcohol wash liquor (75 ml. of glacial acetic acid are mixed with 425 ml. of 95 per cent. alcohol, and the mixture is saturated by shaking with excess of "triple salt") and again centrifuged. Second and third washings are carried out with 5 ml. of ether, and the precipitate is finally dried and dissolved in exactly 10 ml. of 0·1 *N* ammonium thiocyanate solution. The tube is again centrifuged to remove traces of insoluble uranyl phosphate. The yellow colour of the solution is measured in the photoelectric colorimeter, using a blue filter. The presence of ammonium thiocyanate stabilises the colour against temperature changes, but water can be used where a constant temperature can be accurately maintained. For trichloroacetic acid filtrates of serum, 0·5 ml. of the serum is treated with exactly 3·5 ml. of water and 1 ml. of 20 per cent. trichloroacetic acid, and the mixture is stirred and centrifuged. Exactly 2 ml. of the clear supernatant liquid are transferred to a 15-ml. centrifuge tube and treated with 11 ml. of uranyl zinc acetate solution. The further procedure is as described above. The sodium-content of normal urine may be estimated directly by treating 0·2 ml. of urine with 8 ml. of uranyl zinc acetate solution, but protein must be removed by ashing or by treatment with powdered mercuric chloride. Satisfactory agreement between the values calculated and found for serum containing known amounts of added sodium was obtained.

F. A. R.

Spectrographic Examination of the Mineral-Content of Human and Other Milk. H. Dingle and J. H. Sheldon. (*Biochem. J.*, 1938, **32**, 1078–1086.)—Thirty samples of human milk, three samples of fresh cows' milk and twenty-three samples of commercial milk preparations were examined. Contamination during collection of the fresh milks was avoided as far as possible. The samples were dried (where necessary) and gently charred, and the arc spectrum of each specimen was photographed, graphite electrodes being used. In order to ensure that the lines forming the spectra were derived from metals present in the milk and were not due either to contamination during collection and charring or to impurities in the carbon electrodes, an examination was made of milks collected in vessels of copper, rubber, zinc and platinum and charred in crucibles of porcelain, glass, copper, zinc and platinum and examined with electrodes of graphite, copper and zinc. After allowance had been made for the presence of elements that were in all probability derived from one or other of the above-mentioned sources of contamination, the following conclusions were reached:—The elements, in order of spectrographic prominence, that may be regarded as normal constituents of both human milk and the commercial milk foods examined were: calcium, magnesium, sodium, phosphorus, potassium, rubidium, lithium, barium, strontium, manganese, aluminium and zinc. Lead and boron appeared to occur in minute and variable quantity in both human and non-human milk, but the occurrence of copper and iron was doubtful, their presence in commercial milk being almost certainly the result of contamination during processing. Minute traces of molybdenum appeared to exist normally in milk. The following elements were looked for but were not found in pure milk: antimony, arsenic, beryllium, bismuth, cadmium, caesium, chromium, cobalt, fluorine, germanium, gold, indium, iridium, lanthanum, mercury, nickel, niobium, osmium, palladium, platinum, rhodium, ruthenium, scandium, silicon, silver, tantalum, thallium, tin, titanium, tungsten, vanadium, yttrium and zirconium. The human and non-human milks were found to be very similar in their mineral contents, the most conspicuous difference being an excess of potassium in non-human milk, though this may be introduced during the process of preparation. There is more molybdenum and less lead in non-human than in human milk. The prepared milks, unlike the fresh cows' milks, contained silicon, tin and lead; the former contained more iron than the latter. F. A. R.

Determination of Iodine in Sheep Thyroid. J. Sigurjonsson. (*Biochem. J.*, 1938, **32**, 945–948.)—The relatively high iodine contents of human thyroid in Iceland does not necessarily indicate that the soil and water of Iceland are rich in iodine, since the human being is not entirely dependent on food obtained from the soil. The thyroids of sheep, however, would be expected to give an indication of the iodine content of the soil and water where they grazed. Accordingly the thyroids of 33 sheep were dissected out and weighed. The iodine contents of the glands were measured as follows. Each gland was minced, dried and pulverised and 0·2 g. of the powder was mixed with 10 g. of ashing powder (sodium carbonate anhydrous, 353 g.; potassium carbonate anhydrous, 460 g.; potassium nitrate 250 g.) in a nickel crucible and covered with 5 g. of the powder. The crucible was placed in an electric oven and heated carefully until the mixture was white; the ashing occupied about 1¼ hours and a final temperature of 400° C. was attained. The melt was dissolved in water and the solution neutralised with sulphuric acid. After boiling to remove nitrous acid, 1 ml. of sodium bisulphite solution was added, and the solution was boiled to expel sulphur dioxide. Bromine water was then added and the excess of bromine was removed by boiling. After cooling, potassium iodide solution was added and the liberated iodine was titrated with 0·01 *N* sodium thiosulphate solution. Good recovery of added iodine was obtained by this method. The weight of the thyroids of lambs about 5 months old varied from 1·17 to 1·97 g. with an average value of 1·55 g.; the iodine-content varied from 0·2963 to 0·5926 per cent. of dry substance with an average value of 0·3910 per cent. The corresponding figures for the thyroids of sheep aged 17 months or older were:—1·62 to 4·60 g., average 3·13 g.; 0·2392 to 0·6032 per cent., average 0·4023 per cent. The average iodine-content of both groups was 0·397 per cent. The values found are very similar to the iodine-content of the thyroids of sheep from the neighbourhood of Newcastle, and both are higher than figures reported from Ohio and other districts where goitre was not infrequent. It is concluded that the soil of the district from which the sheep were obtained must have been relatively rich in iodine. F. A. R.

New Colour Reaction for Desoxycholic Acid. K. Kaziro and T. Shimada. (*Z. physiol. Chem.*, 1938, **254**, 57.)—When dry desoxycholic acid is warmed at 50° C. with a few drops of benzaldehyde and a few ml. of 75 per cent. sulphuric acid for 5 minutes, the solution acquires a deep red colour with absorption bands at $569 m\mu$ and $503 m\mu$. If then twice its volume of glacial acetic acid is added to the solution, the colour changes to a beautiful green on standing for a short time. This green solution has four absorption bands at $635 m\mu$, $607 m\mu$, $492 m\mu$ and $464 m\mu$. The reaction is almost specific for desoxycholic acid; the only other substances which behave similarly are 3-keto-12-hydroxy-cholanic acid, a synthetic substance, and β-lagodesoxycholic acid of unknown constitution. Anthropodesoxycholic acid changes to blue-violet and hyodesoxycholic acid to reddish-violet when allowed to stand for 30 to 60 minutes after the addition of acetic acid. The following table indicates the behaviour of the cholic acids and related substances when warmed with benzaldehyde and sulphuric acid (reaction 1) followed by addition of acetic acid (reaction 2):—

	Reaction 1	Reaction 2
Desoxycholic acid	Deep red	Green
Cholic acid	Yellowish-red	Reddish-yellow
Glycocholic acid	,,	,,
Hyodesoxycholic acid	Orange red	Pale red
Anthropodesoxycholic acid	Red-brown	Brown
β-Lagodesoxycholic acid	Deep red	Green
3-Keto-12-hydroxy-cholanic acid ..	,,	,,
3-Hydroxy-12-keto-cholanic acid ..	Yellow	Pale red
Dehydrodesoxycholic acid	,,	,,
Reductodehydrocholic acid	,,	,,
3,7-Dihydroxy-12-keto-cholanic acid	,,	Pale yellow
3-Keto-7,12-dihydroxy-cholanic acid	,,	Yellow
β-Dehydrohyodesoxycholic acid ..	,,	,,
Dehydrocholic acid	,,	Pale yellow
Cholesterol	Yellow	Pale red
Cholestenone	,,	Pale yellow
Cholestanone	,,	,,
Palmitic acid	Yellow	Pale red
Stearic acid	Pale yellow	,,
Oleic acid	Brown	Brown
Linolic acid	Dirty brown	Deep brown
Lecithin	Yellowish-red	Pale brown
Urea	Yellow	Yellow
Serum	Red	Pale green

F. A. R.

Silica-Content of Blood. H. Frank and G. Gerstel. (*Z. physiol. Chem.*, 1938, **253**, 225–230.)—Kraut (*Z. physiol. Chem.*, 1931, **194**, 81) described a method of estimating silica in 5 ml. of blood by oxidising with nitric and sulphuric acids, igniting in a platinum crucible and weighing the sulphated ash before and after treatment with hydrofluoric acid. Kraut found the silica-content of blood to be between 0·5 and 1·5 mg. of SiO_2 in 5 ml. This value has now been found to be much too high. A large quantity (100 to 360 ml.) of blood was used in the estimation. This was oxidised with nitric acid, and the residue was ignited and fused with caustic soda and sodium peroxide. The product of the fusion was dissolved in water, and the silica was determined by the customary method. This gave results from 0·025 to 0·16 mg. of SiO_2 in 5 ml. It is shown that Kraut's high results are accounted for by his failure to obtain a constant weight for the sulphated ash before treatment with hydrofluoric acid; the 3 minutes' ignition specified by Kraut is purely arbitrary and quite inadequate. F. A. R.

Inhibition of the Benzidine Blood Test by Ascorbic Acid. R. Kohn and R. M. Watrous. (*J. Biol. Chem.*, 1938, **124**, 163–168.)—The presence of ascorbic acid in urine prevents the formation of the blue colour in the benzidine test for blood. Moreover, the blue colour is rapidly discharged when ascorbic acid is added. Ascorbic acid which had been completely oxidised by potassium permanganate solution also inhibited the reaction and decolorised the blue solution, but in a weaker manner. The interference with the test caused by ascorbic acid may be a serious matter in the examination of urines from patients undergoing ascorbic acid "saturation" tests; it may be avoided by extracting the urine with ether, evaporating the ethereal extract, and applying the test to the residue.
F. A. R.

Determination of Vitamin A with the Photoelectric Colorimeter. W. J. Dann and K. A. Evelyn. (*Biochem. J.*, 1938, **32**, 1008–1017.)—The photoelectric colorimeter devised by Evelyn (*J. Biol. Chem.*, 1936, **115**, 63) has been used for the measurement of the very unstable blue colour produced in the Carr-Price reaction. The instrument, which is a one-cell direct-reading photoelectric photometer equipped with a range of approximately monochromatic light filters, is particularly suitable for this purpose, as a reading can be obtained immediately after the addition of the antimony trichloride solution to the vitamin A solution. It is claimed that the filters are sufficiently selective for the concentration of the coloured substance to be proportional to $-\log_{10} T$, as in the measurement of the extinction coefficient E by means of the spectrophotometer. To avoid confusion with E, which should be used only for spectrophotometric results, the expression L is suggested for determinations made with the photoelectric colorimeter.

$$\begin{aligned} L &= -\log_{10} T \\ &= -\log_{10} G/_{100} \\ &= 2 - \log_{10} G \end{aligned}$$

where T is the per cent. transmission and G the galvanometer reading with the instrument so adjusted as to give a reading of 100 with the tube containing solvent only. In measuring the vitamin A content of an oil, a weighed amount of the oil (saponified, if necessary) is dissolved in a suitable amount of chloroform, and 1 ml. of the solution is transferred to the colorimeter tube. Nine ml. of antimony trichloride solution in chloroform (25 per cent. w/v) are added rapidly from an automatic pipette, and the reading of the galvanometer is noted immediately it becomes steady. The light intensity should previously be adjusted so that the galvanometer reading is 100 when the tube containing 10 ml. of antimony trichloride solution is placed in the path of the beam. The "L value" of the oil, that is, $L^{1\%}_{1\text{cm.}}$ 620$m\mu$, is readily calculated by dividing $L = 2 - \log G$ by the concentration and the thickness of the liquid in the colorimeter tube. By using the appropriate filter, the carotene-content of a solution can be measured in a similar manner. For commercial β-carotene:—

$$L^{1\%}_{1\text{cm.}}\ 440m\mu = 1440 \text{ to } 1640$$
$$L^{1\%}_{1\text{cm.}}\ 620m\mu = 220$$

It was shown by experiment that L was proportional to the amount of vitamin A, the error being only about 2 per cent., that is, solutions when tested in the instrument obeyed Beer's Law. Other experiments showed that the concentrations of the antimony trichloride solution need not exceed 20 per cent., and that the presence of alcohol or water in it did not invalidate the results, as was claimed by Notevarp and Weedon. Stale solutions of the reagent also gave good results. The only difference noticeable between the results obtained when fresh and stale solutions were used was that with the latter fading began immediately, but with the former the colour remained stationary for 10 to 15 seconds and then decreased; the rate of fading was the same with both solutions. The observed value of L was found to be increased by 4 to 5 per cent. for a decrease in temperature of 10° within the range 0° to 30° C. The relations between the "L value" and the generally accepted constants are expressed by the equations.

$$E^{1\%}_{1\text{cm.}}\ 328m\mu = L^{1\%}_{1\text{cm.}}\ 620m\mu \times (0{\cdot}41 \pm 0{\cdot}05)$$
$$E^{1\%}_{1\text{cm.}}\ 620m\mu = L^{1\%}_{1\text{cm.}}\ 620m\mu \times (1{\cdot}30 \pm 0{\cdot}03)$$
$$\text{Blue value} = L^{1\%}_{1\text{cm.}}\ 620m\mu \times (20 \pm 3{\cdot}0)$$

F. A. R.

Spectrographic Studies on the Antimony Trichloride Reaction for Vitamin A. II. Influence of Oxidising Agents on the Reaction. O. Notevarp and H. W. Weedon. (*Biochem. J.*, 1938, **32**, 1054–1063.)—The inhibition of the 693$m\mu$ band obtained in the antimony trichloride reaction for vitamin A is prevented to a great extent by gentle oxidation, but it is difficult to control the removal of the inhibitor, either by controlled oxidation by air or by addition of oxidising agents such as chlorine, antimony pentachloride or bromine before or after adding the reagent. It was found, however, that the use of antimony trichloride solution containing 0·1 g. of bromine per litre gave increased and constant values of $E^{1\%}_{1\text{cm.}}$ 603$m\mu$. In all oils, whether fresh or old, an increase in the blue value was found over and above that obtained by the use of the usual reagent, and the ratio $E^{1\%}_{1\text{cm.}}\ 603m\mu / E^{1\%}_{1\text{cm.}}\ 572m\mu$ increased and more nearly approached the value for the rich concentrate prepared by Carr and Jewell, *viz.* 1·92. With the new reagent,

$$\text{Blue value} = 6{\cdot}5 \times (E^{1\%}_{1\text{cm.}}\ 603m\mu)^{0{\cdot}75}$$

F. A. R.

Vitamin A and the Thyroid. G. Logaras and J. C. Drummond. (*Biochem. J.*, 1938, **32**, 964–968.)—Three groups of rats were fed on a basal vitamin A-free diet, the first group receiving no supplement, the second receiving a dose of 35 I.U. of vitamin A twice weekly, and the third group a daily supplement of 3000 I.U. of vitamin A. Measurements of the basal metabolic rate were made when the animals weighed 150 g. After 80 days on the diets each group of rats was divided into three sub-groups, one to serve as control, the second receiving 19 injections of 100 γ of thyroxine, and the third 15 injections of 2 : 4-dinitrophenol. Basal metabolism studies were made of all the animals. A marked rise in the basal metabolic rate of the rats on the unsupplemented diets and on the diet supplemented with 10 I.U. per day of vitamin A was observed after injection of thyroxine or 2 : 4-dinitrophenol. A similar large rise was observed with the rats receiving 3000 I.U. per day of vitamin A after injection of 2 : 4-dinitrophenol, but the group on the high vitamin A diet showed only a small increase in the metabolic rate after injection of thyroxine. Furthermore, the loss of weight induced by thyroxine treatment was somewhat reduced when the high dose of vitamin A was administered. Estimations of the vitamin A contents of the livers of the animals used in the experiments were made. The results indicated that far from accelerating the depletion of the vitamin A reserves of the liver, administration of thyroxine tended rather to conserve them. F. A. R.

Sensitive Test for Vitamin C. K. V. Giri. (*Mikrochem.*, 1937–38, **23**, 283–285.)—The reduction by vitamin C of potassium ferricyanide to ferrocyanide, which gives a dark red-brown precipitate with a solution of ammonium molybdate reagent, is the basis of a colour test for vitamin C in plant and animal tissue extracts. *Reagents.*—A 0·6 per cent. solution of potassium ferricyanide; a 2·5 per cent. solution of ammonium molybdate in 5 N sulphuric acid; 10 per cent. trichloroacetic acid. When 0·5 ml. of the ferricyanide solution and of the trichloroacetic acid are mixed with 1 ml. of the test solution in a test-tube and 1 ml. of the molybdate solution is added, the colour appears in 2 to 3 minutes. The test is sensitive to 0·02 mg. in 1 ml. of solution. Reducing sugars, cysteine and glutathione in these conditions give no colour, even in concentrations up to 2 mg. per ml. If necessary, tannins and pigments may be removed by treatment with mercuric acetate. The vitamin may be extracted from the material by the method of Birch, Harris and Ray (*Biochem. J.*, 1933, **27**, 590; Abst., ANALYST, 1933, **58**, 490). As a spot test a drop of the test solution is treated on the spot-plate with a drop of ferricyanide solution, followed by a drop of molybdate solution. The limit of identification is 0·5γ in 5 cmm. The test may also be carried out on filter-paper. J. W. M.

Bacteriological

Method for Determining the Action of Certain Organisms on Nitrogen Distribution in Milk. G. H. McFadden and H. H. Weiser. (*Amer. J. Pharm.*, 1938, **110**, 154.)—The method here suggested comprises the following steps: (1) cultivation of the particular micro-organism in skimmed and sterilised milk; (2) precipitation and removal of protein with trichloroacetic acid; (3) determination of the non-protein amino nitrogen in the filtrate by Van Slyke's method; (4) hydrolysis of the same filtrate by heating at 100° C. for 24 hours in an autoclave and determination of the non-protein amino nitrogen after hydrolysis; (5) determination of the total nitrogen in the filtrate. The micro-organisms used were of the genus *Lacto-bacillus*, five cultures of *Acidophylus* were obtained from research laboratories and ten strains were isolated from various dairy products. These organisms were grown in milk at 37° C., for 2, 4, 6 and 8 weeks, and the product was then tested by the method outlined above. The results obtained are summarised in tabular form as follows:—

		Non-protein amino nitrogen in 300 g. of milk			
		Before hydrolysis		After hydrolysis	
Time of incubation at 37° C.	Total non-protein nitrogen in 300 g. of milk (N.P.N.) g.	g.	Per cent. of total N.P.N.	g.	Per cent. of total N.P.N.
2 weeks	0·1069–0·1456	0·0204–0·0387	19–26	0·0476–0·0696	39–45
4 ,,	0·1053–0·1379	0·0327–0·0399	29–31	0·0337–0·0517	32–38
6 ,,	0·1181–0·1353	0·0370–0·0444	31–34	0·0242–0·0406	20–30
8 ,,	0·1121–0·1384	0·0380–0·0653	33–47	0·0194–0·0292	17–19

Heating at 100° C. gave a more complete hydrolysis of those nitrogenous complexes that might be broken down by the organisms in sufficient length of time; hence the quantities shown in the last two columns are progressively smaller as the time of incubation advances. D. R. W.

Effect of Freezing on Bacteria. R. B. Haines. (*Proc. Roy. Soc.*, Ser. B., 1938, **5**, 451–63; *Bull. Hyg.*, 1938, **13**, 176–7.)—In the experimental investigation recorded in this paper aqueous suspensions of young cultures were prepared and subjected to freezing at various rates and storage at different temperatures, and the numbers of living cells were determined before and after such treatment. It was found that with *Ps. pyocyanea* about 80 per cent. of the cells were killed when frozen rapidly with solid carbon dioxide at — 70° C., with *B. coli* about 40 per cent., with the spores of *B. mesentericus* about 27 per cent., and with the spores of *B. cereus* 0 per cent. The rate of freezing, however, was found to have little effect, about the same percentage of cells being killed when the suspensions were cooled at — 70°, — 20° and — 5° C. According to the "mechanical destruction" theory of the effect of freezing the more rapid rate of cooling, by which smaller ice crystals would be formed, should destroy more cells than the slow rate, and the fact that this is not so suggests that this theory is incorrect. Moreover, measurement of the size of cells before and after freezing showed no significant difference, and alternate freezing and thawing failed to show any evidence of disruptive effect. Bacterial suspensions rapidly frozen at — 70° C. and stored at different temperatures below zero showed slow death rate at — 20° C. (25 per cent. of *B. coli* being still alive after 163 days) and rapid death rate at — 1° and — 2° C. (only 4 per cent. of *B. coli* remaining alive at the latter temperature after 11 days). These findings suggest that there is a critical temperature of storage in the frozen state for bacteria analogous to that for muscle and approximating to — 1° to — 2° C. In further investigation of the cause of death by freezing, experiments were made on solutions of bacterial protein. Ninety litres of broth were inoculated with *Ps. pyocyanea* and after cultivation the cells were removed by centrifugalisation and washing with alcohol and ether. Thirty-five g. of dried bacteria were obtained, ground in a ball mill at — 3° C. for 48 hours, and extracted with 1 litre of ice-cold water, and the extract was centrifuged and filtered. The resulting liquid, which contained heat-coagulable protein, was frozen rapidly at — 70° C. and stored at — 20° C. and — 2° C. Measurement of the heat-coagulable protein showed that at — 2° C. about 17 per cent. was precipitated in the first 24 hours and 50 per cent. in 8 days, whilst at — 20° C. the amount precipitated was almost negligible. The author considers it probable that the death of bacteria on freezing is due to denaturation of some of the cellular protein. Rapid freezing with desiccation is used successfully in the preservation of living bacteria (*cf.* ANALYST, **1936**, **61**, 496); the success of this method is probably due to the fact that under such conditions the protein is not denatured. There was no evidence of precipitation of cellular protein with a single freezing and thawing, yet as such treatment gives rise to a high death rate with some bacteria, it is supposed that there is a time lag between incipient denaturation and actual coagulation and that sufficient change in the protein takes place to destroy the vitality of the cell. A similar phenomenon has been observed in the death of muscle. D. R. W.

Toxicological

Application of Electrodialysis in Toxicological Analyses. R. Fabre. (*J. Pharm. Chim.*, 1938, **27**, 467–476.)—*Method.*—The electrodialyser recommended consists of three concentric compartments, the outer one being a glass crystallising dish, 12 cm. in diameter, and the inner ones formed by two glass collars, respectively 9 and 6 cm. in diameter, slightly belled-out around the bottom edge and fitted with membrane bottoms. The membranes are of cellophane, a suitable quality weighing 60 g. per sq. m.; the material is soaked in water and fitted by tying a little way up the side of the collar. The 9-cm. collar with membrane stands on glass tubes laid in the crystallising dish, and the 6-cm. collar with membrane similarly stands on glass tubes laid in the 9-cm. collar; the glass tubes are connected with the water supply and serve the dual purpose of cooling tubes and supports. The outer compartment is filled with distilled water in which is immersed a circular anode of platinum foil about 5 cm. in diameter placed parallel with the bottom; the leading wire of the anode is sealed in a glass tube. The intermediate compartment contains an aqueous suspension of the finely divided organ under examination. The inner compartment is partly filled with distilled water and contains another circular platinum-foil electrode serving as cathode. A P.D. of 120 volts D.C. is applied. After a few minutes, gassing occurs at the electrodes and a current of several milliamperes passes. The current gradually increases and becomes steady at about 120 to 180 milliamperes in about 15 to 20 minutes. Subsequently the current falls off as ionised substances are removed from the intermediate compartment.

Fluorine in Blood and Organs.—Electrolysis is carried out for 15 hours. The contents of the anode compartment containing the fluorine (about 150 ml.) are drawn off, and replaced with water, and the electrolysis is continued for a further 3 hours. This second anode liquid is then drawn off and combined with the first. The liquid, which is acid, is neutralised with sodium hydroxide, and evaporated almost to dryness on a water-bath. The fluorine is distilled off as hydrofluosilicic acid by the method of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, **1933**, **5**, 7;

Abst., ANALYST, 1933, **58**, 242), and subsequently determined colorimetrically by de Boer's alizarine-zirconium method (*Chem. Weekblad*, 1924, **21**, 404; Abst., ANALYST, 1924, **49**, 497). Tests were carried out on the various parts of rabbits, to the food of which sodium fluoride had been added; the largest amounts of fluorine recovered were from the teeth. [The method of pretreatment of teeth prior to electrodialysis is not given.]

Barbiturates.—The suspension of the finely divided organs is made slightly alkaline (*p*H 9·2) with diethylamine, and electrolysis is carried out for 48 hours. The barbiturate is found in the anode liquid associated with inorganic anions from which it may be separated by extraction with chloroform, and organic impurities, for the removal of which the author's vacuum micro-sublimation method is applicable (*J. Pharm. Chim.*, 1933, **18**, 417) preferably after mixing the dried residue with magnesia and employing a temperature of 160 to 190° C. A possibility exists that some barbiturate may become decomposed in the anode compartment during the electrolysis. This may be avoided by immersing the anode in a separate vessel containing potassium sulphate solution, connection being made with the "anode" compartment of the electrodialysis cell by a potassium sulphate bridge. Tests were made with the aid of the method of the distribution, among the various organs, of veronal and epivan administered intravenously; the highest amounts found were in the thyroids and suprarenals. S. G. C.

Agricultural

Evaluation of Some Soil Fungicides by Laboratory Tests with *Phymatotrichum omnivorum*. W. N. Ezekiel. (*J. Agric. Res.*, 1938, **56**, 553–577.)—*Phymatotrichum omnivorum* is a fungus responsible for root rot, and spreads from plant to plant by growing from root to root, infected roots being located from a few inches to 8 or more feet underground. Materials commonly used as soil fungicides have not proved effectual in eradicating it. The methods used in the present tests were: (1) Toxicity tests that allowed the materials to act on the fungus without interposition of soil. The fungicides were volatilised through air and cotton plugs before coming in contact with the fungus inoculum. Pentachloroethane, tetrachloroethane, xylene and ammonia were the most toxic substances tried against *Phymatotrichum*. (2) Tests of the materials in moist soil to determine their ability to penetrate soil. Jars were filled with neutralised moist soil, inoculum of the fungus was added, and growth observed through the glass walls; this was made possible owing to the characteristic strands of *Phymatotrichum omnivorum* growing to a greater extent along the glass-soil surface than into the soil. When fungicides were mixed mechanically in the soil a number of organic mercury compounds, particularly ethyl compounds, were surprisingly effective in preventing growth, but this initial effectiveness diminished after 5 weeks' contact with the soil to a value to be expected from their mercury-content, and they were ineffective when applied on the surface with a buried inoculum. Such volatile materials as pentachloroethane, tetrachloroethane, xylene, carbon disulphide, turpentine, perchloroethylene, trichloroethylene and dichloroethylene, applied in the proportion of 100 p.p.m. to the soil surface in closed jars completely inhibited growth in inoculum 135 mm. deep, but formaldehyde was ineffective even at a concentration of 4000 p.p.m. When the inoculum was inserted deeply in a moist soil treated on the surface 4 to 8 weeks previously with pentachloroethane, the effectiveness of the compound was found to have been reduced to between a fifth and a tenth of the original value. The 100 p.p.m. application of penta- and tetrachloroethane and xylene required to be increased to 500 to 1000 p.p.m. under adverse conditions, such as a very compact soil. These three compounds are suggested as promising soil fungicides for field trials.

D. G. H.

Total Composition of Derris Extract. R. S. Cahn, R. F. Phipers and J. J. Boam. (*J. Soc. Chem. Ind.*, 1938, **57**, 200–209.)—The composition of derris root extract depends partly on the variety and the strain within the variety, and partly on the method of cultivation. The commercial roots are of two types: *Derris elliptica* and *D. malaccensis*, the extract from which contains 15 to 45 per cent. of rotenone, and the "Sumatra-type" (Cahn and Boam, *J. Soc. Chem. Ind.*, 1935, **54**, 42T) which gives an extract containing 2 to 5 per cent. of rotenone. The *l*-toxicarol content of derris extract varies inversely with the rotenone-content, and ranges from about 50 to 60 per cent. for Sumatra-type extract to very low figures, certainly not more than 10 per cent., for rotenone-rich extracts. *l*-α-Toxicarol and sumatrol appear to occur generally in derris, and examination of the evidence brought forward by various workers leads the authors to agree with the conclusion of Haller and LaForge (*J. Amer. Chem. Soc.*, 1934, **56**, 2415) that deguelin exists in derris extract, partly, at least, in the laevorotatory form. A mixture of crystalline dehydro-compounds has also been isolated from derris extract; these are present in only small quantity and appear to be insecticidally valueless. Derris extracts contain appreciable quantities of fats or waxes and small quantities of acids. The authors give their estimated composition of derris extract of three types—Sumatra-type, medium (20 per cent.) and high (40 per cent.) rotenone-content—in the following table. No great accuracy is claimed for these figures.

Ingredient Per Cent.	High rotenone-content	Medium rotenone-content	Sumatra type
Rotenone	40	20	2–5
l-Toxicarol	About 8	Nearly 25	50–60
l-Deguelin	27	27	12
Sumatrol	?	A little	15–5
Fats, waxes and acids ..	10	10	10
Total accounted for ..	85	82	89

It is pointed out that in the biological testing of insecticides in suspension the particle size of the insecticide must be rigidly controlled, as this factor greatly affects the insecticidal power. The literature on the quantitative examination of derris extracts is discussed, and the authors give in detail their own methods for determining the separate constituents of the extracts.

E. M. P.

Organic

Determination of Glycerol and Some Other Hydroxylated Compounds. S. H. Bertram and R. Rutgers. (*Rec. Trav. Chim., Pays-Bas*, 1938, **57**, 681–687.)—A method for the determination of glycerol has been based on its power to form a complex with copper in alkali solution, and it is claimed that the method is free from the defects of previous methods based on the same principle. A quantity (not exceeding 10 ml.) of the crude glycerin containing not more than 800 mg. of glycerol is weighed into a 100-ml. stoppered measuring flask and water is added to bring the volume to 10 ml. Ten ml. of a solution containing 30 g. of sodium hydroxide in 100 ml. are added, followed by 60 ml. of ethyl alcohol (methylated spirit of 96 to 97 per cent. by vol. containing 5 per cent. of methyl alcohol may be used) and, after mixing, sufficient of a 10 per cent. alcoholic solution of cupric chloride is added to give a clearly visible, permanent precipitate of cupric hydroxide. The liquid is then made up to the mark with alcohol and about 60 ml. are centrifuged for 10 minutes. Fifty ml. of the clear solution are pipetted into a 300-ml. Erlenmeyer flask and in succession 100 ml. of water, dilute sulphuric acid (1 part of conc. acid to 6 parts of water by vol.) in sufficient quantity to render the solution slightly acid, and about 10 g. of potassium iodide are added. The mixture is titrated with 0·1 *N* sodium thiosulphate solution until a colourless solution is obtained, 1 ml. = 9·1975 mg. of glycerol. A blank determination is made and the titration value is subtracted. For very accurate work the volume of the precipitate in the measuring flask can be taken into account by measuring the volume of the precipitate in the centrifuge tube and taking 50 per cent. of this as the true solid phase. As standards for testing the method, good pure tristearin and pure refined oils and fats were used. To determine the glycerol yield of fats, 25 g. are saponified by boiling for 1 hour with a solution of 6 g. of sodium hydroxide in 100 ml. of alcohol, water is added, and the mixture is acidified with dilute hydrochloric acid. The separated fatty acids are dissolved in petroleum spirit and removed, and the glycerol-containing solution is evaporated to about 100 ml. filtered, neutralised with dilute sodium hydroxide solution, and weighed, and an aliquot portion is taken for the determination. Lower fatty acids did not interfere with the determination nor did a slight rise in temperature, but a fall in temperature was liable to cause crystallisation of the copper-sodium-glycerol complex from a concentrated solution. The analysis of two technical samples of crude glycerin yielded results agreeing closely with the factory results, but with a third sample the result was 86·5 against 90·1 per cent., owing probably to the presence of a considerable quantity of trimethylene glycol. Glucose, sucrose, lactose and small quantities of trimethylene glycol have little effect on the results, but reduction due to reducing sugars must be completed before centrifuging, and for this purpose the solution must be kept at room temperature for at least one hour before centrifuging. If the presence of impurities which might consume iodine is suspected, the amount of complex-bound copper may be determined by diluting 50 ml. of the solution with 50 ml. of water, acidifying, rendering slightly alkaline, and boiling until most of the alcohol is evaporated and the copper is precipitated. After filtration and washing, the precipitate is dissolved in dilute sulphuric acid to which a little bromine has been added, the mixture is boiled until excess of bromine has disappeared and then cooled, and the titration is carried out after addition of potassium iodide. A fermentation glycerol, analysed by this method in less than an hour, yielded 1·39 per cent. of glycerol, as against 1·32 per cent. by the conventional method, which took 2 days. The method may be adapted for other hydroxylated compounds soluble in dilute sodium hydroxide solution or in alkaline alcohol if they contain at least 2 hydroxyl groups in suitable adjacent positions. With mannitol, sorbitol and tartaric acid the copper complex is insoluble in alcohol, and a 10 per cent. aqueous copper sulphate solution may replace the alcoholic cupric chloride solution. D. G. H.

Distribution of Hexadecenoic Acid in Natural Fats. T. P. Hilditch. (*Rec. Trav. Chim., Pays-Bas*, 1938, **57**, 503–508; *Cf.* Hilditch and Jasperson, *J. Soc. Chem. Ind.*, 1938, **57**, 84–87; Abst., ANALYST, 1938, **63**, 442.)—The older idea that hexadecenoic acid was confined to marine animal oils is now superseded, and the general percentage distribution of the acid in natural glycerides has been found to be approximately as follows:—Aquatic vegetable life, 25–30; fish (freshwater), 18–25; fish (marine), 10–15; frog, 15; lizard, 10–12; bird (domestic fowl), 7; rat, 7–8; cow (liver glycerides), 12, (depot), 2·5–3, (milk), 3–4; pig (depot), 9, (liver glycerides), 2·5–3. Vegetable fats: soya-bean (seed), 2; palm (fruit coat), 1; olive (fruit coat), 1; arachis (seed), 1; cotton seed (seed), 1; teaseed (seed), 0·8. Thus, hexadecenoic acid is a major component in fats from the lower forms of life, but is present only in very small amounts in the depot fats of animals and the fats of plants at the opposite end of the evolutionary scale. D. G. H.

New Croton Seed from Nyasaland. (*Bull. Imp. Inst.*, 1938, **36**, 151–153.)—The croton seeds examined came from the tree identified as *Croton megalobotrys* Muell. Arg. (= *C. gubonga* S. Moore); they were flat and ovoid, nearly 1 in. long, 0·8 in. broad and 0·5 in. thick, and averaged 2·4 g. in weight. The thin brittle woody shell (37·4 per cent.) enclosed cream-coloured kernels (62·6 per cent.) which contained 5·0 per cent. of moisture and 47·3 per cent. of a golden-yellow clear oil of nutty flavour. The oil had the following characteristics:—sp.gr. at 15·5/15·5°, 0·9292; n_D^{20}, 1·4756; saponification value, 196·5; iodine value (Wijs ½ hour) 129·2; acid value, 1·5; unsaponifiable matter, 0·9 per cent. It would appear from previous work on the bark and seed of *C. gubonga* (Goodson and Clewer, *J. Chem. Soc.*, 1919, 923T) that the oil has some purgative effect, a property possessed in more marked degree by the oils from the allied species of *C. tiglium* and *C. elliotianus*. The only use for the oil in this country would appear to be for soap. D. G. H.

Seed Oils of Indian and Australian Sandalwood Trees. W. V. Kotasthane and N. Narayana. (*Agric. Coll. Mag., Poona*, 1938, **29**, No. 4.)—The Indian sandal seed oil from Mysore has already been described (Iyer, ANALYST, 1935, **60**, 319; Srinivasaya and Narayana, *J. Indian Inst. Sci.*, 1936, **19**, 1), and the present investigation compares the ether-extracted seed oil from Indian sandalwood (*Santalum album*) with that of the Australian sandalwood (*Eucarya spicata*). The Australian oil was yellowish-red and the Indian dark brown. The latter contains a high proportion of unsaponifiable matter which separates as a resinous mass during alcoholic saponification. The oil was treated with acetone, which dissolved it, leaving a white sticky resinous mass. The characteristics of (*a*) the Indian oil, (*b*) the Indian oil de-resinified, and (*c*) the Australian oil were as follows:—sp.gr. 25–25°, (*a*) 0·9325, (*b*) 0·9292, (*c*) 0·9522; n_D^{25}, (*a*) 1·4762, (*b*) 1·4732, (*c*) 1·4753; saponification value, (*a*) 177·65, (*b*) 184·25, (*c*) 196·85; iodine value, Hanus, (*a*) 141·85, (*b*) 116·4, (*c*) 108·25; acetyl value, (*a*) 20·53, (*b*) 20·98, (*c*) 42·43; thiocyanogen value, (*a*) 71·45, (*b*) 36·62, (*c*) 52·13; Reichert–Meissl value, (*a*) 3·2, (*c*) 7·19; solid acids, per cent., (*b*) 50·07, (*c*) 6·86, with iodine values, (*b*) 107·7, (*c*) 99·87; iodine value of liquid acids, (*b*) 111·9, (*c*) 111·9. The high iodine values of the solid acids are regarded as possibly due to the presence of iso-oleic or elaidic acid. Both seed oils dissolve sulphur on heating, the reaction with the Indian oil being violent; both thicken on exposure to light and air, and both dissolve resins such as dammar or copal, giving a varnish which on drying yields a glossy elastic transparent film. The resinous mass obtained with acetone from the Indian oil (about 8 per cent.) is soluble in carbon tetrachloride and chloroform, insoluble in benzene, acetone and alcohol and miscible with the original oil. It contains neither nitrogen nor phosphorus and is highly unsaturated, having an iodine value (Hanus) of 202, and it combines with iodine to form an insoluble compound. It dissolves sulphur, reacting violently with it, and when spread over any surface, yields a glossy unbroken film in 24 hours. D. G. H.

New Colour Reaction for Oxalic Acid. M. Paget and R. Berger. (*J. Pharm. Chim.*, 1938, **27**, 577–579.)—In a mixture of the sample (*e.g.*, 5 ml. of a 0·01 per cent. solution of oxalic acid) with 1 to 2 ml. of conc. hydrochloric acid is inserted a strip of pure zinc (weight, 1 to 2 g.) in such a way that the strip is in contact with the column of liquid over its whole length. The solution is then boiled for 1 minute, and 2 minutes after removal of the flame the liquid (which contains glyoxylic acid produced by the reduction of the oxalic acid, *cf.* Pesez, ANALYST, 1937, **62**, 145) is transferred to a test-tube containing 5 drops of a 1 per cent. solution of phenylhydrazine hydrochloride. The mixture is then heated almost to boiling, and cooled well under running water (important). On addition of an equal volume of pure conc. hydrochloric acid (to prevent the subsequent precipitation of zinc ferricyanide) and 5 drops of a 5 per cent. solution of potassium ferricyanide, a currant-red colour develops rapidly on shaking; this is Fosse's modification of Schryver's reaction. Other oxidising agents (*e.g.* hydrogen peroxide, per-salts or chlorates) may replace the ferricyanide, but are less effective, although 2 drops of a 20-vol. solution of hydrogen peroxide should be used if iron is present. It has been shown that no glyoxal is produced under the conditions specified, and acetic, formic, succinic, lactic, tartaric, malic, citric, cacodylic and methylarsinic acids do not interfere with the test. If, however, nitric, methylarsinic or cacodylic acid (which are all reducible by hydrogen) is present, the reduction process should be prolonged by about 5 minutes. Sulphuric, hydrobromic, hypobromous and phosphoric acids, and sodium, lithium, potassium, calcium or ammonium ions do not affect the reaction, which will detect 0·02 mg. of oxalic acid in a 0·001 per cent. solution. J. G.

Note on the Cineole Method for the Determination of *o*-Cresol. Submitted by the Standardisation of Tar Tests Committee. (*J. Soc. Chem. Ind.*, 1938, **57**, 212.)—A note draws attention to the revised figures that will appear in the revision of the British Standard Specifications for refined cresylic acids, and in the second edition of "*Standard Methods for Testing Tar and its Products.*" The standard method stipulates that in the determination of the crystallising point 8·40 g. of the sample and 12·00 g. of pure cineole (crystallising point, 1·2 to 1·4° C.) shall be weighed into the inner tube, which is 25 mm. in diameter; this method gives for the mixtures crystallising points that are 0·4 to 0·7° C. higher than those published in the original account of the method (*J. Soc. Chem. Ind.*, 1932, **51**, 59T). Mixtures containing *o*-cresol and *m*-cresol, or *o*-cresol and *p*-cresol alone give slightly abnormal results, the degree of variation from the revised normal curve for the two limiting cases being shown in the table below.

	Crystallising point with cineole		
o-Cresol per cent.	*o*-Cresol + commercial refined cresylic acid ° C.	*o*-Cresol + *m*-cresol ° C.	*o*-Cresol + *p*-cresol ° C.
100	56·4°	56·4°	56·4°
95	54·7°	—	—
90	53·0°	53·5°	53·0°
85	51·35°	—	—
80	49·6°	50·4°	49·4°
75	47·7°	48·75°	47·45°
70	45·8°	46·9°	45·35°
65	43·7°	—	—
60	41·5°	42·8°	40·85°
55	39·15°	—	—
50	36·7°	38·3°	35·5°
45	34·1°	—	—
40	31·0°	32·9°	29·0°

The crystallising points of the materials used were: *o*-cresol 31·0°, *m*-cresol 11·5°, *p*-cresol 34·7°. In order to obtain accurate results with abnormal or synthetic mixtures of *o*-cresol admixed with either *m*- or *p*-cresol alone it is advisable to prepare a crystallising-point curve for mixtures of known *o*-cresol content with the phenols present in the sample. Mixtures of *o*-cresol and phenol alone give crystallising points with cineole in close agreement with the standard curve. The nitration method for determining *m*-cresol, together with a study of the distillation range and the specific gravity of the sample, will usually give an approximate idea of the composition and of the presence or absence of phenol and xylenols.

E. M. P.

Onocerin. J. Zimmermann. (*Helv. Chim. Acta*, 1938, **21**, 853–859.)—Onocerin was extracted from the finely-ground roots of *Ononis spinosa* by the method of H. Schulze (*Z. physiol. Chem.*, 1936, **238**, 35), and the diacetate derivative was prepared by heating it with acetic anhydride. After recrystallisation, the diacetate had the formula $C_{34}H_{52}O_4$, m.p. 224° C. and $[\alpha]_D + 29{\cdot}4°$; saponification produced a diol, $C_{30}H_{48}O_2$, m.p., 202° to 203° C. Oxidation of a solution of the onocerin in glacial acetic acid with chromic acid, followed by concentration of the solution by distillation *in vacuo* and dilution with water, yielded onocerin diketone, which could be crystallised from alcohol (m.p., 185° C.); the action of a hot solution of hydroxylamine acetate for 30 minutes in an alcoholic solution produced the dioxime, $C_{30}H_{46}O_2N_2$, m.p., 236° C. On acetylation of the diol obtained by saponification (m.p., 225° C.) glistening needles of the diacetate (m.p. in an evacuated capillary tube 260° C.; $[\alpha]_D + 100°$) were obtained. J. G.

Inorganic

Use of Adsorption Indicators in Acidimetry and Alkalimetry. S. N. Roy. (*J. Indian Chem. Soc.*, 1938, **15**, 165.)—The applicability of adsorption indicators in acidimetry and alkalimetry has been described by the author where fluorescein was used as the adsorption indicator in conjunction with lead and tin salts (*id.*, 1936, **13**, 486; 1937, **14**, 120). A trace of bismuth subnitrate with fluorescein may be used in the titration of nitric acid with sodium carbonate or sodium hydroxide solutions. The equivalence point is marked by a colour change from green to yellow (with sodium carbonate) or green to reddish-yellow (with sodium hydroxide). The method is only suitable for titrating nitric acid solutions above $N/5$ in strength, as the bismuth salt is not sufficiently soluble in weaker acid solutions. Eosin may be used in place of fluorescein, the colour-change being from dull red to scarlet. The colour-change results from adsorption of the dye on the precipitated bismuth salt formed on neutralisation of the acid. S. G. C.

Effect of *p*H Value in Precipitations with 8-Hydroxyquinoline. H. V. Moyer and W. J. Remington. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 212–213.)—The separation of zinc from magnesium, and also of iron from aluminium, by means of 8-hydroxyquinoline, was studied. It was found that, whilst precipitation of the magnesium compound begins at *p*H 7·5, a partial precipitation of this compound begins at *p*H 5·5 when the zinc hydroxyquinoline compound is being precipitated in the liquid. Serious co-precipitation of magnesium with zinc occurs unless the *p*H is kept at least 2 units of *p*H lower than the value at which magnesium alone is precipitated. Iron can be separated from aluminium provided that the *p*H of the solution is kept between 3·5 and 4. Experiments on co-precipitation were carried out with solutions containing the same amount of iron but with increasing amounts of aluminium, the *p*H of each being adjusted to 4·1, a value at which the aluminium compound tends to precipitate only in the presence of iron. It was found that with more than a certain amount of aluminium present, a further increase in the amount did not result in any further increase in the quantity of aluminium compound co-precipitated with the iron compound. This behaviour was interpreted to mean that the co-precipitation of the aluminium compound was due to adsorption on the surface of the iron compound. Analogous results were obtained with zinc precipitated in the presence of magnesium. The *p*H values were determined, by means of a glass electrode, in the filtrates cooled to room temperature. S. G. C.

Modified Permanganate Volumetric Method for the Determination of Antimony in Commercial Lead and High-Lead Alloys. R. G. Myers. (*Philippine J. Sci.*, 1937, **64**, 365–371.)—The well-known permanganate titration method for antimony in alloys is liable to give low results when applied to alloys containing a large proportion of lead, say, over 80 per cent., owing to the accumulation of large quantities of lead sulphate, which tend to occlude antimonious sulphate. In the following modified method the solvent effect of ammonium acetate on lead sulphate is utilised to reduce the occlusion effect. A 1-g. sample is mixed with 15 ml. of conc. sulphuric acid and 5 g. of potassium bisulphate in a 500-ml. conical pyrex flask, and the whole is allowed to digest overnight on a hot-plate. The mixture is then boiled for 10 to 12 seconds over a bunsen flame. The insoluble sulphates should not have a dark colour. After cooling, 15 ml. of water are added. The clear liquid (A) is decanted into another similar flask, and the residue is washed by decantation with two 25-ml. portions of 10 per cent. tartaric acid solution, the washings being received with the main liquid, to which are added 10 ml. of conc. hydrochloric acid. The lead sulphate residue is heated with 40 ml. of 33 per cent. ammonium acetate solution until completely dissolved; 30 ml. of water are added, and the solution (B) is reserved. Liquid (A) is boiled for one minute and 10 ml. of conc. hydrochloric acid are added, after which solution (B) is added, the flask being rinsed with 40 ml. of water. The combined liquids are cooled in ice to 5° to 8° C. and titrated in the usual way with $0{\cdot}1\,N$ potassium permanganate solution; the pink colour at the end-point should persist for 8 to 10 seconds. In a range of test-experiments with upwards of 0·2 per cent. of antimony present, the largest error was − 1·6 per cent. With less than 0·2 per cent. of antimony the accuracy is lower and the method becomes impracticable. A micro-burette graduated to 0·01 ml. is necessary when the antimony-content is below about 6 per cent. (on 1 g. of the sample). S. G. C.

Determination of Gold and Silver in Cyanide Solutions. W. E. Caldwell and L. E. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 318–319.)—The method is claimed to be simple and applicable to large volumes of solution. It is based upon conversion of the cyanide into ferrocyanide and precipitation of the noble metals, together with mercury, by magnesium. Two litres of cyanide liquor are treated with ferrous sulphate (10 times the weight of cyanide present), 50 ml. of saturated mercuric chloride solution, 5 g. of magnesium powder, and 60 ml. of strong hydrochloric acid. Cautious addition of the acid is necessary to prevent frothing. After standing overnight the clear liquid is siphoned off, and the precipitate is collected on a filter, into which 20 g. of granular test lead are sprinkled during the process of washing. The dried residue is removed as completely as possible from the filter and placed on a cupel containing a concave layer of test lead. A little more lead (making about 45 g. in all) is wrapped in the filter, which is placed on the charge in the cupel. The latter is cautiously introduced into a hot muffle in order to burn the paper and drive off the mercury without loss. The residue is cupelled, and the silver and gold are determined in the button in the usual manner. Alternatively, the paper and mercury are eliminated in a scorifier, the lead being first scorified and then cupelled. W. R. S.

Precipitation of Calcium in Presence of Molybdate and Iron. R. C. Wiley and A. Yedinak. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 322–323.)—The procedure serves for the determination of phosphoric acid and calcium in the same portion of solution, the phosphorus being first removed as ammonium phosphomolybdate. Five g. of fine powder (dried skim milk, meat or fish meal, meat scrap, etc.) are mixed with 0·5 g. of sodium carbonate, and slowly heated in a basin until a carbon-free ash results. The ash is dissolved in a mixture of 30 ml. of nitric acid and 5 ml. of hydrochloric acid, both strong, the basin being heated on a steam-bath. Phosphorus is determined in the solution as usual, by precipitation with excess of molybdate mixture. The filtrate is rendered slightly ammoniacal and then treated with strong acetic acid (2 ml. excess); an excess of ammonium oxalate is added during constant stirring, and the solution is boiled until the calcium oxalate settles readily. After standing overnight the precipitate is collected, washed with water and dissolved in dilute sulphuric acid, and the solution is titrated with permanganate solution. Iron in moderate amounts does not interfere. Accurate results are claimed for the method. W. R. S.

Reaction of Sulphur. L. van Itallie. (*J. Pharm. Chim.*, 1938, **27**, 465–467.)—Elemental sulphur in small quantities (even less than 1 mg.), produces a blue colour with a mixture of sodium hydroxide solution (4 *N*) and pyridine. The colour gradually changes to green, and, if there is much sulphur present, to brown. Acetone, in place of pyridine, gives a similar reaction. Warming the liquid favours the development of the colour. Yellow ammonium sulphide gives a green colour with pyridine and a greenish-yellow colour with acetone, but sodium sulphide produces no colour. The nature of the coloured substances is unknown.
S. G. C.

Simultaneous Conductometric Titration of Sulphuric and Nitric Acids. C. J. van Nieuwenburg. (*Rec. Trav. chim.*, 1938, **57**, 616–619.)—Conductometric titrations of mixed solutions of sulphuric acid and nitric acid with standard baryta solution were carried out. During the titration the conductivity decreases through two causes: (1) the disappearance of $H^{\cdot}$ ions from the solution, (2) the disappearance of SO_4'' ions as insoluble barium sulphate. As soon as all the sulphuric acid has been precipitated only the first cause remains. It was found that the neutralisation point of the sulphuric acid in this simple titration was difficult to locate, chiefly because the effect of the conductivity of the highly mobile $H^{\cdot}$ ions completely predominated over that of the much less mobile SO_4'' ions. This difficulty could be overcome by suitable buffering to reduce the $H^{\cdot}$ ion concentration to such an extent that it no longer blurred out the effect of the SO_4'' ions, but not to so low a value as to make the titration of the nitric acid impossible. Sodium monochloroacetate proved satisfactory; the amount added was not critical, several times the amount equivalent to the mineral acids present being suitable. A complication lay in the slow precipitation of the barium sulphate from the aqueous liquid, but this difficulty was overcome by adding ethyl alcohol to the solution. A concentration of 50 per cent. of alcohol by volume was the most suitable. The liquid was stirred by passing through it a current of air, free from carbon dioxide, the air supply being stopped during each reading of the galvanometer. It was found advisable to carry out the titration slowly, waiting one minute after each addition of 1 ml. of *N*/10 baryta solution. The first inflexion of the curve relating galvanometer readings to volumes of baryta solution indicates the end-point of the sulphuric acid titration.

S. G. C.

Microchemical

Qualitative Micro-Method for the Identification of Alkyl Groups Linked with Oxygen or Nitrogen. Micro-Zeisel Method. I. M. Furter. (*Helv. Chim. Acta*, 1938, **21**, 872–879.)—A disadvantage of the Zeisel method in its usual form is that it affords no information as to the nature of the alkyl group present. Attempts to overcome this difficulty (*cf.* W. Kuster and M. Maag, *Z. physiol. Chem.*, 1923, **127**, 190) have been made by forming a derivative of the alkyl group which may be identified (*e.g.* by its m.p.); the author finds that the derivatives hitherto suggested are difficult to crystallise when present in small quantities, and particularly from mixtures, as they are then oily in nature. He describes a modified all-glass form of Pregl's micro-Zeisel apparatus, in which an inclined tube containing fine granules of calcium chloride held in position by wads of glass-wool, is interposed between the washing device and the receiver; this is used because water accelerates the decomposition of the derivative formed subsequently (see below). The outlet of the apparatus is a narrow vertical tube, which passes to the bottom of a dry wider vertical reagent-tube having thick walls and a constriction near the top and containing a suspension of the silver salt of 3·5-dinitro-benzoic acid (see below) in absolute ether. Evaporation of the ether is minimised by immersing the reagent-tube in ice, and packing glass wool around the inlet tube at the constriction. The sample (10 to 30 mg.) is heated with 2 ml. of hydriodic acid (sp.gr. 1·7) in the distillation flask, 2 platinum tetrahedra being added to facilitate smooth boiling; carbon dioxide gas is passed through the system continuously. The wash-bottle contains a suspension of phosphorus in sodium thiosulphate and cadmium sulphate solutions, which serves to remove iodine, hydriodic acid and hydrogen sulphide. If the substance under investigation does not decompose readily, or if the alkyl iodide has a high b.p., heating must be prolonged and a more rapid stream of carbon dioxide is used; an extreme case is octyl iodide (b.p. 236° C.), which requires 2 hours. It has not yet been possible to obtain completely quantitative results with such substances, and for qualitative purposes it is necessary only to obtain sufficient of the iodide to produce an identifiable compound with the silver salt in the receiver. When the distillation is finished the receiver is removed, with the gas stream still passing, sealed at the constriction, and then placed (suitably protected) in a water-bath for 2 hours at 100° C.; an electric bomb-oven providing temperature-control to within ± 3° over the range 50 to 150° C. is described as an alternative, or when the pressure developed inside the receiver is exceptionally high, an autoclave may be used. This heating operation ensures that the reaction of the alkyl iodide with the silver salt is complete. The receiver is then cooled and opened, and the contents are filtered off and washed, three 2-ml. portions of ether being used for washing. The filtrate (15 ml.)

is washed in a separating funnel in succession with 15 ml. of a 1 per cent. alkali solution, with hydrochloric acid and finally with water, and then dried for 1 hour over sodium sulphate. If only one alkyl group is to be identified, the solution may now be evaporated and the m.p. of the residue determined, the method of mixed m.p., or a determination of the carbon-content, being used for confirmation. Otherwise the residue is recrystallised from pentane or benzene, a solution of it in 0·1 to 2 ml. of ether being then mixed with an excess of a conc. solution of α-naphthylamine in 80 per cent. alcohol. The mixture is filtered, and the precipitate is washed with the alcohol and recrystallised from pentane or petroleum spirit. Fractional crystallisation from solvents such as pentane, benzene, methyl or ethyl alcohol or mixtures of these has enabled two or three alkyl groups to be identified when present together. The silver salt of 3·5-dinitrobenzoic acid is prepared by neutralising a solution of a commercial sample of "pure" 3·5-dinitrobenzoic acid in 50 per cent. alcohol with 0·1 *N* sodium hydroxide solution, with litmus paper as indicator, one drop more of the acid being then added so as to make the reaction weakly acid again. A solution of the calculated quantity of silver nitrate in water is then added, and the precipitated silver salt is separated, washed with alcohol and ether and dried over phosphorus pentoxide at 50° C. under reduced pressure. It is unchanged on storage in the dark over phosphorus pentoxide for one month. A table in the original paper gives the m.p. of the esters of the dinitrobenzoic acid and of the α-naphthylamine compounds corresponding with 22 alkyl-groups. A selection from this follows:—*Iso*-propyl, 121° to 122°, 143° to 144°; *tert.*-amyl, 117° to 118°, 123° to 124°; benzyl, 113° to 114°, 117° to 118°; methyl, 110° to 111°, 121° to 122°; ethyl, 92° to 93°, 120° to 121°; *n*-propyl, 74° to 75°, 103° to 104°; *n*-butyl, 61° to 63°, 92° to 93°; *iso*-amyl, 60° to 61°, 104° to 105°, *n*-octyl, 60° to 62°, 48° to 49° C., respectively. J. G.

Salts of Complex Cations for the Microscopic Detection of Anions. III. 1·2-Dinitritotetramminocobaltic Nitrate (Flavocobaltic Nitrate). H. A. Hynes and L. K. Yanowski. (*Mikrochem.*, 1937–38, **23**, 280–283.)—Flavocobaltic nitrate, prepared according to Bilty, Hall and Blanchard (*Laboratory Methods of Inorganic Chemistry*, 2nd Ed., p. 179. New York, 1928) used in saturated aqueous solution (about 0·1 *M*) was tested for its reaction with various anions in 1 per cent. solution; one drop each of the reagent and of the test solution were placed together on a microscope slide. The following anions give characteristic reaction products:—bisulphate, bisulphite, carbonate, chromate, dichromate, dithionate, fluosilicate, persulphate, selenate, silicotungstate and sulphosalicylate. The crystals obtained with chromate, dichromate, dithionate and silicotungstate are sufficiently characteristic to be useful for the detection and identification of these anions. Twelve photomicrographs are given. J. W. M.

Colorimetric Micro-Determination of Zinc. W. L. Lott. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 331–333.)—The method utilises 5-nitroquinaldinic acid, which precipitates zinc from feebly acid solution. Reduction with stannous chloride furnishes a deep-orange soluble compound suitable for colorimetric work. For the determination of zinc in soils, the ash is extracted with hydrochloric acid or fused with potassium bisulphate, and the zinc is separated from interfering elements by means of hydrogen sulphide. The zinc sulphide is dissolved in hydrochloric acid, and an aliquot portion of solution (5 to 10 ml.) containing 0·05 to 1 mg. of zinc is made just alkaline to methyl red with 3 *N* ammonia. The solution is re-acidified with 1 to 2 drops of acetic acid, heated almost to boiling, and treated with a slight excess of the reagent (0·75 g. dissolved in 100 ml. of warm 95 per cent. alcohol; 1 ml. precipitates approximately 1 mg. of zinc). After standing on a hot plate without boiling for 30 minutes, the liquid is filtered through an asbestos filter-stick, and the beaker and filter are washed 5 times with boiling water. The precipitate is dissolved in 5 ml. of hot stannous chloride solution (12·5 g. of the salt dissolved in 100 ml. of strong hydrochloric acid and diluted to 500 ml.), the liquid is boiled, and any asbestos fibres are removed by filtration. The cold solution is matched, preferably in a photoelectric colorimeter, against standards prepared by the same process. Very accurate results were obtained. 5-Nitroquinaldinic acid precipitates silver, lead, mercury, copper, iron, cobalt and nickel; hence these metals interfere with the zinc determination. Ammonium and sodium chlorides at concentrations higher than 0·7 *N* cause the zinc precipitation to be incomplete.

W. R. S.

Quantitative Drop Analysis. X. Determination of Sodium. R. Lindner and P. L. Kirk. (*Mikrochem.*, 1937–38, **23**, 269–279.)—Amounts of sodium ranging from 0·13 to 4·13γ have been determined in salt solutions and biological materials, with a standard error of a few tenths of 1 per cent. The sodium is precipitated as sodium zinc uranyl acetate, and the uranium in the precipitate is determined volumetrically by reduction with metallic cadmium to the quadrivalent state and titration with standard ceric sulphate solution to the sexavalent state. Extreme care is necessary to prevent contamination. *Reagents.*—(1) Zinc uranyl acetate solution prepared according to Barber and Kolthoff (*J. Amer. Chem. Soc.*, 1925, **50**, 1625), filtered before use. (2) Wash solution: 95 per cent. alcohol saturated with sodium zinc uranyl acetate, filtered absolutely clear through a Jena G 5/3 glass filter or a glass filter covered with fine asbestos. (3) Asbestos, washed, ignited and ground: Italian asbestos, boiled in successive portions of ceric sulphate solution acidified with sulphuric acid and stored in glass. (4) Five per cent. sulphuric acid; both acid and water redistilled in glass. (5) Standard ceric sulphate solution made approximately 0·01 *N* and standardised against pure sodium oxalate or against pure potassium ferrocyanide. (6) Indicator solution: either 0·0025 *M* phenanthroline ferrous sulphate, or a 0·1 per cent. aqueous solution of setopaline C (Miller and van Slyke, *J. Biol. Chem.*, 1936, **114**, 583). (7) Spirals of metallic cadmium made by cutting a thin ribbon from a stick of cadmium with a lathe tool; this helix flattened to a disc has an area of about 2 sq. cm. This reduction agent can be used almost indefinitely; cadmium amalgam and other reductors are not so effective. All distilled water is redistilled in glass. *Detail.*—The sample, free from proteins and phosphate, is measured with a capillary pipette into a porcelain micro-titration dish. The dish is placed on a micro hot-plate, and a magnetic thread stirrer is inserted. The solution is evaporated almost to dryness, and 1 ml. of zinc uranyl acetate reagent is added. The mixture is stirred, warmed for about 5 minutes, and left in a moist dust-free atmosphere for 12 to 24 hours (shorter times are insufficient). For the filtration a small sintered glass filter-stick, covered with asbestos, is used. The precipitate and asbestos are removed to the dish with a drop of 5 per cent. sulphuric acid, and the filter-stick is rinsed with water. The dish is placed on the micro hot-plate, and the metallic cadmium and the thread stirrer are introduced. The liquid is stirred and warmed for 5 minutes, the cadmium is then removed and washed, and the solution is titrated with ceric sulphate, a micro-capillary burette being used. It is convenient to add excess of ceric sulphate solution and titrate back with standard ferrous ammonium sulphate solution in the presence of either of the indicators mentioned. A blank determination must be carried out and the correction applied. *Biological material.*—Organic matter is destroyed by ashing at 450° C., and phosphate is removed by precipitation with solid calcium hydroxide and centrifuging after standing 2 to 4 hours. The method is so sensitive that plasma should be diluted 1 : 100 with water before sampling. J. W. M.

Possible Source of Error in the Determination of Nitrogen by the Micro Dumas Method. H. J. Ravenswaay and A. Schweizer. (*Rec. Trav. chim.*, 1938, **57**, 688–693.)—In the course of analysis by the micro Dumas method it was found that there are substances which yield a gas that is not nitrogen. Thus, humin formed as a by-product in the preparation, by Tollens' method, of levulinic acid by the dehydration of pure sucrose with hydrochloric acid, showed a content of 0·5 to 2·4 per cent. of nitrogen, despite the fact that all the substances used in its preparation were free from nitrogen. Investigation showed that the gas was methane. Occasional statements in the literature that the results obtained in the Dumas method are rather high may be attributable to this phenomenon. In a separate test, in which a slow current of pure methane mixed with carbon dioxide was passed through a Dumas apparatus, a considerable amount of the methane remained unoxidised and collected in the azotometer. The analysis of humin by the Ter Meulen or Kjeldahl methods gave negative results for nitrogen. It was concluded that it is advisable to analyse the evolved gas when making a nitrogen determination by the micro Dumas method, and at the same time the nitrogen-content of the substance should be checked by an independent method, the Kjeldahl method for example. S. G. C.

Colorimetric Micro-Determination of Iron. Application to Biological Products. R. Paulais. (*Compt. rend.*, 1938, **206**, 783–785.)—The compound of ferric iron with cupferron, whilst insoluble in dilute acids, is readily soluble in chloroform, yielding a yellow solution. This solution, examined by Meunier's electrophotometer (*Bull. Soc. Chim. biol.*, 1936, **19**, 113), was found to be strongly absorbent in the blue region of the spectrum, most absorption occurring with $\lambda = 420 m\mu$: with this wave length, 2 to 50γ of iron as the cupferron compound in 10 ml. of chloroform could be determined to within 0·4γ. A second measurement was made in the green ($\lambda = 480 m\mu$); the absorption measured corresponded with the same quantity of iron as that found in the blue. The apparatus is standardised with solutions containing known amounts of iron. The best procedure for obtaining the colorimetric solution is to add to the aqueous acid solution containing the iron a few drops of hydrogen peroxide and 0·5 ml. of a freshly-prepared 5 per cent. solution of cupferron. The liquid is well shaken and extracted three times with small quantities of chloroform; in the third extraction a few drops of cupferron are also added. The chloroform solution is diluted to 10 ml. and the coloration is measured with the electrophotometer. Of the other elements precipitated in acid solution by cupferron, molybdenum, titanium and tin do not interfere, as their cupferron compounds are only very slightly coloured; moreover, they are not often present to any great extent in biological materials; the copper compound gives a solution only about one-fiftieth as intensely coloured as the iron compound, and thus any error due to copper should ordinarily be negligible. The principal interest of the method lies in the non-interference of phosphate, as little as 10γ of iron having been almost quantitatively recovered in the presence of 1 g. of disodium hydrogen phosphate. Biological materials are preferably ashed and the iron determined in the extract of the ash in dilute sulphuric acid. Following wet oxidation with sulphuric acid and nitric or perchloric acid, it is desirable to neutralise the sulphuric acid with ammonia and acidify the liquid to give an acid strength of 2 *N*.

S. G. C.

Physical Methods, Apparatus, etc.

Spectroscopic Method for the Identification and Determination of Small Quantities of Benzene. Application to the Determination of Benzene Vapours in an Atmosphere. P. Laurin. (*J. Pharm. Chim.*, 1938, **27**, 561–577.) —Existing physical methods for the determination of benzene are based on refractometry or on adsorption by activated carbon or silica gel, and, consequently, are not specific. The author therefore prefers to determine the optical densities of the maxima of the ultra-violet absorption curves by means of the apparatus of Fabre and Amy (*id.*, 1935, **22**, 5). It is considered advantageous to use solutions of benzene in 95 per cent. alcohol rather than to obtain the spectra of benzene vapour, because the former are more conveniently obtainable in toxicological work (*cf.* Henri, *J. Phys. Radium*, 1922, **3**, 181) and are recovered unaltered subsequently, and so can be used for further tests. The source of light used was a water-cooled, quartz-enclosed hydrogen lamp operated by a 1500- to 2000-volts supply, and its intensity could be varied by means of a rheostat; it gave a continuous spectrum over the range 270 to 220$m\mu$. The solution to be tested was contained in a cell having parallel quartz faces, the distance between which could be varied from 0·01 to 20 mm., and this was placed between the hydrogen lamp and the spectrograph, which enabled a spectrum 215 mm. long to be obtained. A high-frequency spark apparatus was used to obtain the emission spectrum of iron (which was used as a reference standard of wave-length), and it enabled wave-lengths to be measured to within 0·1$m\mu$ in the region 230$m\mu$ (0·4 to 0·5$m\mu$ in the region 400$m\mu$). The actual Fabre and Amy apparatus for measuring the absorption consisted of 27 quartz plates, 0·5 mm. thick, inclined at different angles to the plane of the incident light, and arranged in such a way that the intensity of the radiations striking them was decreased by the constant fraction which was eliminated by reflection. The plates were carried in slides in such a way that they could be interposed singly or in groups between the spectrograph and either the cell containing the sample or a similar cell containing 95 per cent. alcohol only. The procedure therefore, was to produce alternately on the same photographic plate the spectra of the sample and of the pure solvent, after rendering them weaker by the interposition of a variable number of the quartz-plates. Thus, at points where the two spectra are equal, the optical density of the solute (benzene) corresponds with that of the quartz plates, a small correction for the wave-length being applied. Anti-halo gelatin-silver bromide plates are recommended, and formulae for developing and fixing solutions are given in the original paper; the times of exposure varied from 10 to 600 seconds, according to the number of quartz plates used. In qualitative work, maxima corresponding with 260·7, 254·0, 248·2 and 243·0$m\mu$ were perceptible to the unaided eye when derived from 0·05 per cent. solutions of benzene. These were less easily seen as the concentration was decreased to 1 in 20,000, although by the use of a Sannié recording microphometer (*Compt. rend.*, 1934, **198**, 1149) all 4 bands could be detected at dilutions of 1 in 100,000; 0·1 mg. of benzene is required in such circumstances. If the concentration exceeds 0·05 per cent. the bands overlap, and it is then necessary to dilute the solution with alcohol. For quantitative work the wave-length is plotted (as abscissa) against the optical density (*i.e.* the logarithm of the ratio of the intensities of the incident and transmitted radiations), the latter being determined from the number of quartz plates required to obtain the same degree of darkening with the solvent as with the solution to be tested; in practice, however, it is simplest to determine the wave-lengths of zones of equal optical densities, and to plot the results only in the regions of the maxima and minima. In the author's apparatus this is facilitated by the fact that 11 exposures may be made on one plate, which thus serves to determine the rough outline of the curves, whilst a second plate is used for the intermediate points; this ensures a sensitiveness of about 5 per cent., even for the highest optical densities. Preliminary work demonstrated that 0·001 to 0·020 per cent. solutions of benzene in alcohol followed the Lambert–Beer law (*i.e.* for a given thickness of solution, the optical density was proportional to the concentration), so that the apparatus had only to be calibrated initially in terms of solutions of benzene of known concentrations. If the quartz-plate device is not available the method may still be used, solutions of benzene in alcohol of known concentration being used instead. The concentration of benzene in alcohol which produces the same optical density as the solution being tested, for the same wave-length, is then found by the method of trial and error. The error is 5 per cent. for the concentrations 0·025 to 0·050 per cent. (thickness of layer, 20 mm.); 2 to 5 mg. of benzene in 10 ml. of solution may be determined. Luszczak (*Wien. Med. Woch.*, 1936, **86**, 91, 150) has shown how the method may be adapted to the analysis of mixtures of benzene and xylene, toluene and xylene, or all three, by comparing the absorptions due to those bands which are common to the solvents under examination with those which are not. The method of Lebeau and Damiens (*Ann. Chim.*, 1917, **8**, 221) was adapted to the extraction of benzene from an atmosphere before the spectroscopic determination. A measured volume of the vapours to be tested was dried (interfering substances being removed if necessary by suitable absorbing agents), and bubbled through the alcohol in refrigerated containers. Condensation at —85° C. by means of a mixture of carbon dioxide snow and acetone was used, and in the presence of alcohol the benzene was dissolved immediately and completely. An apparatus for this purpose is described. J. G.

Reviews

GAS ANALYSIS. By A. McCULLOCH, M.Sc.Tech., A.I.C., A.Inst.P. Pp. 166, 38 illustrations. London: H. F. & G. Witherby, 1938. Price 7s. 6d. net.

As the author explains in his preface, this book is written primarily for students taking laboratory courses in fuel technology. It is accordingly advisedly selective rather than comprehensive. The selection is excellent, although a slight regret may be felt that no space is given to any of the physical methods which now play so important a part in technical gas analysis. The main question, however, in assessing a book of this type, is whether or not it provides a clear and sufficient guide to the analyst for those processes with which it claims to deal, and here the answer is a decidedly affirmative one. The book will certainly be of great use, not only to the students for whom it is designed, but also to practising analysts.

Chapter I (17 pp.) deals with cleaning of mercury, maintenance of apparatus and measurement and sampling of gas. Chapter II (12 pp.) describes absorbents used in gas analysis. The use of phosphorus as supplementary to pyrogallate or hydrosulphite "with a view to removing the final traces of oxygen" (p. 33) is not always reliable; in fact, the converse procedure may sometimes be necessary (*cf.* ANALYST, 1934, **59**, 593). It is also not clear what justification there is for prohibiting the use of potassium hydroxide purified by alcohol for making up alkali solutions (p. 29). Chapter III (14 pp.) deals with determination by combustion; the author's experience as an instructor enables him to decide with authority the necessary amount of space to devote to the algebra of combustion volume-relations. The treatment of this subject seems both adequate and duly succinct. Some kindred matter occurring later (pp. 83–4) might perhaps have been included with advantage in this chapter. Chapter IV (56 pp.) deals with five selected types of gas analysis apparatus, namely those of Bunte, Orsat, Buckley and Sinnatt, Bone and Wheeler, and Haldane. The description of the Buckley and Sinnatt apparatus in a text-book is to be welcomed. The same chapter also includes descriptions of some special instruments for the determination of carbon monoxide; these might perhaps have been better included in the succeeding chapter (25 pp.) on miscellaneous determinations. Chapter VI (16 pp.) deals with calorific value. "Nm^3" is a convenient abbreviation for cubic metres at N.T.P., dry, and may well be popularised; it is a pity that the British units have no equally convenient accepted abbreviations. Recording gas calorimeters are not described, presumably, because such expensive pieces of mechanism do not usually come the way of students of fuel technology. A useful appendix (12 pp.) is given; the first table (corrections for temperature differences, mainly for use with the Bone-Wheeler apparatus) is not quite self-explanatory and should have a fuller heading. The table of average compositions of various technical gases (pp. 154–5) is very useful.

The print is of agreeable and readable size, and is attractively set out. The type, however, appears to have been badly worn in many places, or else something has gone wrong in the process of printing. In a few places there seem to have been typographical difficulties, as in the frequently occurring formula C_nH_{2n+2}, where the levels of the foot-characters are rather variable, and the plus sign is unduly large. The paper, being thick and well-glazed, is well-chosen for a laboratory manual, which is liable to get splashed; the cover is strong and neat, and, although a trifle dour in appearance, is likewise suited to laboratory conditions.

Such adverse criticisms as it has been possible to make are very minor ones; the book, as a whole, is most useful and interesting, and Mr. McCulloch is to be congratulated on it.

H. R. AMBLER

A BRIEF INTRODUCTION TO THE USE OF BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE. By ERNEST HAMLIN HUNTRESS, Ph.D. Second Edition. Pp. x + 44. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 5s.

To every organic chemist Beilstein is a formidable necessity and its "facile use" a desirable attainment. This formidability lies not only in the language, but also in the inevitable complexity of the comprehensive scheme of classification adopted in the Fourth Edition of Beilstein's famous work. Dr. Huntress's book is a successful attempt to overcome these obstacles.

The first three chapters are devoted to a general explanation of the broad outline of Beilstein's system, and Chapter IV to the arrangement of derivatives of individual index compounds. In the next chapter the somewhat troublesome question of tautomeric substances is adequately treated. Chapter VI is devoted to the location of compounds from structural formulae. Many examples are given, and these will well repay careful study. The uninitiated will learn, surprisingly enough, that the apparently "obvious" classification is not always the one used by Beilstein; for example, β-chlorethyl chloroacetate is listed as a functional derivative not of ethyl acetate but of chloroacetic acid. The book closes with 121 examples for practice.

To have explained in so short a space the mysteries of Beilstein is no mean achievement, and the author is to be congratulated on his success. Since, too, the study of Beilstein's classification is in itself an education in organic chemistry, Dr. Huntress's book is worthy of careful perusal by all interested in advanced organic chemistry.

HAROLD TOMS

SELECTED TOPICS IN COLLOID CHEMISTRY. By ROSS AIKEN GORTNER. Pp. xiii + 169. Ithaca: Cornell University Press; London: Humphrey Milford, Oxford University Press. 1937. Price 11s. 6d.

This book, dedicated to W. D. Bancroft, covers the contents of a series of lectures delivered in the Department of Chemistry of Cornell University during the first semester of the academic year 1935–1936, when the author held the George Fisher Baker Non-Resident Lectureship in Chemistry.

The Preface states that "no claim is made that the present volume is an adequate treatment of the nature and behaviour of colloid systems. On the other hand, it is specifically designed to present an introduction to certain fundamental phenomena characteristic of such systems and, above everything else, to present the author's viewpoint and interpretation as to how and why these phenomena should be of interest to biochemists, physiologists, and biologists."

The eight chapters are preceded by a reprint of the author's Public Lecture, "Scientific Genealogy," a delightful account of the author's early teachers and their scientific ancestors, with some intimate personal reflections. The chapters are successively entitled: The Beginnings of the Science; What is Colloid Chemistry?; Some Basic Concepts; Some Fundamental Properties of Colloid Systems; Electrokinetics; Surface Tension, Surface Energy, Interfacial Tension, and Molecular Orientation; Adsorption; The Water Relationships of the Biocolloids. The book is illustrated with 35 text figures and 38 series of tabular data, which are critically discussed in the text. Adequate author and subject indexes are also provided. The book is well printed and bound and is quite a handsome volume.

Chapter I reveals Gortner as an enthusiastic admirer of Thomas Graham, and he repeatedly quotes Graham's papers from 1830 to 1864, revealing how well and truly Graham laid the foundations of modern colloid chemistry and to how great an extent his terminology has survived.

The next three chapters are deliberately condensed to the bare essential details necessary for the understanding of the phenomena in the remaining four chapters, which deal with the special research interests of the author himself.

Gortner has long been recognised as an authority on electrokinetics, interfacial tension and molecular orientation, and the water relationships of the biocolloids. These chapters are the most valuable in the book and deserve study by all interested in colloid chemistry, especially if working with biological materials. The discussion on "bound" water is extraordinarily complete and surveys ten different methods which have been used by various investigators to study the state of water in hydrophilic colloid systems. Of very real importance is this question of "bound" water—that part of the water in hydrophilic sols and gels which is immobilised or at least differs in its physical properties from bulk water.

Specialised as is this volume, it will repay study for the clarity and conciseness in its treatment of important fundamentals. Two illustrations must suffice to demonstrate the author's style and his critical attitude. Page 33, "It should be emphasised that in the above discussion the phrase, 'critical zone' and the words 'stable' and 'unstable' are used in a relative sense, for in all colloid studies *time* must be considered as a fourth dimension. Time is just as important in defining conditions of colloid study as is concentration, and in many instances it is more important than is temperature."

Page 68, "The fact that syneresis occurs on ageing indicates very definitely that gels do not remain in an equilibrium state and accordingly are not amenable to physico-chemical treatment which presupposes the existence of a state of equilibrium. This is a fact which has often been overlooked, *i.e.* that gels are dynamic and not static colloid systems, and that attempts to deal with them as though all constituents were in complete equilibrium are likely to lead to erroneous conclusions."

The reviewer strongly recommends this little work. WILLIAM CLAYTON

A SHORT MANUAL OF SYSTEMATIC QUALITATIVE ANALYSIS BY MEANS OF MODERN DROP REACTIONS. By Prof. Dr. C. J. VAN NEUWENBURG and Dr. G. DULFER. Third Edition. Pp. 96. Amsterdam: D. B. Centen's Utg. Maatschappij (N.V.). 1938. Price 3.75fl.

The second edition of this work was reviewed in this journal in 1936 (ANALYST, **61**, 150), and in view of the fact that the third edition is identical, nothing need be added to the former review. The reason for the absence of any alteration is given in the preface: "Awaiting the publication of the Report of the Committee on New Reagents of the International Union of Chemistry, which will give us a better survey of the available spot tests, we thought it best to introduce no new reactions." This edition is essentially the same as the second. The abbreviation "c.c." has been replaced by "ml." JANET W. MATTHEWS

MODERN RUBBER CHEMISTRY. By H. BARRON. Pp. 330 + Indexes. Hutchinson's Scientific and Technical Publications, Ltd. 1937. Price 18s.

This book is "an effort to put forward the scientific principles of rubber manufacture as at present understood." It is a creditable effort, but the author was surely a little too optimistic in expecting to cover this subject in about 300 pages of demy 8vo. The result is that nearly everywhere the treatment is inadequate, and the book fails as a work of reference, although it may find a use among students beginning to study the subject and others interested in gaining an insight into the technical side of the industry.

The science of rubber is completely embraced (the title is inadequate) in the orthodox manner, in twenty-five chapters, the last of which is devoted to the analysis of rubber. The author says of this chapter that "the following outline does not substantially differ from existing schemes," and again, therefore, the account given may be some use to students or others not yet acquainted with the subject, but hardly to anyone else. The account given of the various determinations does not appear to contain any recommendations resulting from practical experience but reads rather as a series of abstracts from the literature. Hence the impression left upon the reviewer is that this book does not meet any particular need.

The volume is well printed and contains separate author and subject indexes.

W. H. STEVENS