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BERNARD SHIRLEY DYER

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

PHYSICAL METHODS AND BIOLOGICAL METHODS GROUPS

A JOINT meeting of these two Groups was held on Thursday, January 29th, in the Barnes Hall of the Royal Society of Medicine, London, W.1. The subject of the meeting was "Methods of Penicillin Assay—their Purpose, Scope and Validity." An afternoon session beginning at 2.30 p.m. dealt with Chemical and Physical Methods. It was presided over by Dr. Amos, the Chairman of the Biological Methods Group, who in his opening remarks emphasised that the meeting was concerned with the purpose, scope and validity of the methods, not their details. The following four papers were read: "Introductory Survey," by E. Lester Smith, D.Sc., F.R.I.C.; "Determination of Individual Penicillins," by W. R. Boon, B.Sc., Ph.D., F.R.I.C.; "Hydrolytic Method," by S. J. Patterson, B.Sc., A.R.I.C., and W. B. Emery, B.Sc., A.R.I.C.; "Spectroscopic Methods," by G. H. Twigg, B.Sc., Ph.D., and a discussion followed.

After an interval for tea an evening session, dealing with Biological Methods of Penicillin Assay, began at 5.30 p.m., and was presided over by Dr. J. G. A. Griffiths, Chairman of the Physical Methods Group. The following papers were read: "Introductory Survey," by N. G. Heatley, M.A., Ph.D.; (*a*) "Serial Dilution Method," (*b*) "Differential Assay by Charcoal Adsorption," by C. G. Pope, D.Sc.; "Turbidimetric Methods," by C. R. Bond, M.Sc. (Tech.), F.R.I.C., and O. L. Davies, M.Sc., Ph.D. The proceedings closed with a brief summing up by Dr. A. A. Miles, Head of the Department of Biological Standards of the Medical Research Council.

The papers read at this joint meeting will be published in the April and May issues of THE ANALYST and reprints containing them all will be published at an early date.

POLAROGRAPHIC DISCUSSION PANEL

A meeting of the Polarographic Discussion Panel of the Physical Methods Group was held in the Concert Hall, L.C.C. Norwood Technical College, London, S.E.27, on Friday afternoon, December 12th, 1947, when a discussion on "The Validity of the Ilkovic Equation in Polarographic Analysis" was opened by Mr. F. L. Steghart.

DEATH

WE regret to record the death of Samuel Russell Trotman.

Obituary

DR. BERNARD DYER

BERNARD SHIRLEY DYER was born in London on February 26th, 1856, the only son of J. A. Dyer, a then well-known London journalist.

He was educated at the City of London School, a fortunate choice for at that time it was the only school in the country that afforded, in addition to chemical lectures, opportunities for practical laboratory work which, however, meant the sacrifice of half-holidays. Dyer seized these opportunities and must have shown an aptitude and liking for chemistry since, on leaving school, he became pupil-assistant in the laboratory of Dr. Augustus Voelcker, consulting chemist to the Royal Agricultural Society. The laboratory proved to be a nursery for Presidents; besides Dyer himself, three of his fellow workers, J. A. Voelcker, E. W. Voelcker, and Alfred Smetham were destined to become Presidents of our Society. Dyer supplemented his daily laboratory work with courses of lectures at the School of the Pharmaceutical Society, King's College and the Royal College of Science and later took the London B.Sc. degree.

His work in Voelcker's laboratory naturally gave him a strong bias towards agricultural chemistry, maintained to the end of his life. For many years he contributed articles on

elementary agricultural chemistry to agricultural periodicals and the lay press and he was in frequent demand to give lectures or open discussions at meetings of Farmers' Clubs or Agricultural Societies. In 1880 he qualified as a "recognised" teacher by passing the Science and Art Department Honours Examination in "Principles of Agriculture" and was then appointed lecturer in this subject at the City of London College where he gave Winter Courses of evening lectures which were well attended by farmers, market gardeners and others interested in agriculture. Prior to this lectureship he had been appointed consulting chemist to the Devon County Agricultural Society and later to the Essex and Leicestershire Agricultural Societies and to various local Farmers' Clubs and Chambers of Commerce. The analytical work arising from these appointments was carried on in a laboratory established by Dyer at the remarkably early age of 21, at 17 Great Tower Street, London, E.C.; these premises were continuously occupied by Dyer and his partners until destroyed in an air raid in 1941, when the practice was removed to 20 Eastcheap.

Dyer did much original work on the growth of crops and on the influence of fertilisers on crop yield, the results of these investigations being published in the Journal of the Royal Agricultural Society and in Annual Reports to the Essex Agricultural Society. His most outstanding contribution to agricultural chemistry perhaps was his clear demonstration that the amounts of phosphoric acid and potash in soils, available for plant growth can be most accurately estimated by using a 1 per cent. solution of citric acid for extracting these constituents from the soil. This demonstration was based on long and laborious investigations of root-sap acidity and on analyses of the soil of twenty-two plots at Rothamsted on which barley had been continuously grown for forty years under varied conditions of manuring; a record had been kept of the manuring and crop yield of each plot, giving direct evidence as to which of the plots were or were not suffering from insufficiency of available phosphoric acid or potash or both. The results of the Rothamsted experiments were embodied in a paper read before the Chemical Society; the unusual length of the paper—nearly fifty pages—is evidence of its value and the University of London awarded Dyer the D.Sc. degree. The citric acid method was widely adopted and still holds its own, at any rate for phosphoric acid.

Dyer subsequently made a long and exhaustive study of the phosphoric acid and potash contents of the wheat soils of Broadbalk Field, Rothamsted, the results of which were published in the *Transactions* of the Royal Society. In 1900 he was deputed by the Lawes Trust Committee to deliver the then triennial Course of Rothamsted American Lectures. These lectures were delivered at Newhaven, U.S., at a meeting of the Association of Agricultural Colleges and Experimental Stations and were published by the United States Department of Agriculture in Bulletin 106 of the Office of Experimental Stations in 1902, under the title of "Results of Investigations of the Rothamsted Soils," and aimed at giving in collective form an account of all the chemical work hitherto carried out in this direction by Gilbert and his various co-workers.

A course of field experiments on the manuring of vegetables and fruits was carried on during a period of twenty years. The work of the first eight years was recorded in the Journal of the Royal Horticultural Society and in the Journal of the Ministry of Agriculture; a full account of the twenty years' experiments was issued as a separate publication in 1924, on "*The Manuring of Market Garden Crops*," but this is now out of print.

Dyer held numerous public appointments: Agricultural Analyst for the Counties of Bedford, Cornwall, Dorset, Essex, Hants, Herts, Leicester, Rutland, Somerset and West Suffolk. Joint Public Analyst for the Counties of Essex, Herts, Leicester, Rutland and Wilts, for the County Borough of East Ham and for the Boroughs of Barking, Dagenham, Ilford, Leyton, Wanstead, and Walthamstow. He was also Official Analyst to the London Corn Trade Association.

He published numerous papers in THE ANALYST on subjects arising from his work as Public Analyst. The last of these (in collaboration with J. H. Hamence) on "The Determination of Nitrogen in Mixed Fertilisers containing Nitrates and Chlorides" appeared in 1938 when Dyer was over eighty years of age. It is remarkable that, despite the demands of a large consulting and analytical practice, he found time for so much original investigation and still more remarkable that he gave so much time in the service of various chemical organisations. He became a Fellow of the Chemical Society in 1875 and served on the Council in 1893–1897 and 1904–1908. He was an original member of the Society of Chemical Industry and Chairman of its London Section in 1923 and 1924. He was elected an Associate of the Institute of Chemistry during the year of its formation and became a Fellow in 1880, served

on the Council for various periods between 1888 and 1929, including two years as Vice-President, and was an Examiner in the years 1899–1903 and 1915–1923. One of the writers first met Dyer during his former term as Examiner and has a very pleasant memory of his kindly and sympathetic attitude towards examinees suffering from "nerves." He also served as one of the Institute's Censors in 1919–1924.

His services to our Society were unique in its history. He was elected an Associate member (a grade long since extinct) at the first regular meeting of the Society in 1875 and a Member in the following year. He became a Member of Council in 1880 and, in 1883, Honorary Secretary (jointly with the late Otto Hehner), in which office he continued for fourteen years and was then elected President (1897–1898). After his retirement from the Presidency he continued to serve on the Council as a Past President until his death nearly fifty years later. He was in his 90th year when he attended his last Council meeting and during the subsequent two years of his life his advice on Society affairs was frequently sought and gladly given. In 1932 he collaborated with Dr. C. A. Mitchell in writing "*Fifty Years of the Society of Public Analysts.*"

Dyer was married twice, first to Alice Collett and secondly, in 1890, to Edith Steel who survives him with two of their three daughters. He died on February 12th within a few days of his 92nd birthday and, by the wish of the family, the funeral at Golders Green was attended only by relatives and intimate friends.

He will be remembered by a large circle of friends not only for his services to the science and profession of chemistry but for his kindliness and readiness to help others less fortunately placed than himself. His life's work speaks for itself and will remain as an enduring monument.

Although Dyer had a special bent for agricultural chemistry, his consulting and analytical practice was of extraordinary variety. A notice of his scale of fees which he must have had printed in the eighties, when he was probably about thirty years old, indicates the wide scope of his practice. Indeed, in those days, so far as analytical chemistry was concerned, he might, without undue exaggeration, have said "I have taken all knowledge to be my province." His tremendous energy and vitality sometimes left those associated with him in the laboratory rather "breathless," but he won their admiration and respect by his profound chemical knowledge and their affectionate regard by his sterling character.

Bernard Dyer was a great lover of Charles Dickens and knew his books almost by heart. It is difficult now to know whether the reading of Dickens moulded that part of his quiet humour which delighted in the bizarre and the odd, or whether this latter characteristic accounted for his love. But the "tuppeny" attendant at the cab rank in Great Tower Street —the double of Dickens's Silas Wegg—would always touch his hat when he saw him, and wish him good-day; while the owner-manager of a certain restaurant buried in one of the City alleys, whose particular business acumen lay in his invariable question to the customer when making out his bill as to whether he had had butter with his roll of bread, always greeted "the Doctor" with great respect. His knowledge of London was like that of Sam Weller. Often, during the course of business which involved walking with a companion in the City, he would pause thoughtfully and then digress from chemistry into a City church with some special beauty or interest known only to the elect; or turn into a quiet square elegant in its ancient pride but tucked away only a few feet from a crowded and noisy street, passing from his purposed course to admire the handicraft of a bygone age. Thus was one of the writers first introduced to the Roman Baths in the Strand, to one of Wren's little-known churches in Queen Victoria Street and to a wonderful Elizabethan red brick house in a cobbled square in Great Tower Street. His memory of odd and humorous occasions was very tenacious and two or three of them may be recalled here.

An elderly lady, who called to see him about suspected poisoning, produced a Bible from her reticule and stated that the name of the poison was in that book but in no event would she tell the name. Another client, who also brought a case of suspected poisoning, produced a piece of meat so far decomposed as to be positively poisonous in its odour, and who explained the reason for his delay in asking for an analysis by stating that the meat had been kept for him until he "came out" and he had only just done so.

It was the custom when the laboratory work pressed to send out for luncheon in order to save time. During the course of an interview with a very special client, one of the laboratory boys broke in to say loudly, that "boiled babies heads" were "off," this description being applied by the boys to a particularly delectable small steak pudding.

He had a great sense of sociability; indeed he often used the description "clubbable" as a sort of sociability classification when speaking of some one or other of his colleagues. It is probable that this tendency was the product of those early days in his professional career when he enjoyed nothing better after a formal meeting than a talk for the purpose of really getting the meat off the bones of some matter under discussion, frequently with the aid of tobacco and beer. In his early days, too, he played the violin with some proficiency, but this ability appears to have diminished or disappeared in later years, although he always seized any opportunity to attend a musical event. The only other indoor recreation to which he was in any way strongly attached was the game of chess—and in this he was moderately proficient. As to his outdoor activities, he was a keen fly-fisher, and even as late as the middle of the war he had London searched for suitable flies for some trout fishing that he was then offered. Scarcely a year passed without at least a few days' fishing somewhere. Apart from this, however, only golf appealed to him; and the appeal was not very great because his club really knew him for his social abilities and his ever-ready help in keeping the grass green and free from worms.

At the time of his death Bernard Dyer was the oldest member of the Savage Club, the members of which had combined together a year or so previously to do him a special honour.

LEWIS EYNON
GEORGE TAYLOR

BERNARD DYER—AN APPRECIATION

WHEN I received a letter from the Editor stating that the Publication Committee of THE ANALYST would like an appreciation of the work of Dr. Bernard Dyer, the reply was "Of course." If this notice could have been written by one of Dyer's contemporaries such as the Voelcker brothers, Otto Hehner or several others, a more satisfactory account of his work would have been given than I can hope to achieve. I plead in mitigation of any shortcomings that Dyer had been a personal friend for fifty years and that I have been a member of the Society of Public Analysts for over forty years.

The Society owes so much to Dyer that the older members cannot think of it without remembering him. He performed an invaluable service to the Society in writing "*Some Reminiscences of its First Fifty Years*," which was published in 1932 in one volume with "*A Review of its Activities*" by C. Ainsworth Mitchell and indexed by Miss Elliott (the "O.G.") —two other old friends whose memory one treasures with gratitude.

This book originated in a request made to Dyer at a dinner given on the occasion of his personal jubilee in the Society. I was unfortunately unable to attend this function but Dyer sent me a complimentary copy of the book and in the accompanying letter expressed "the hope that some of the chatter in the earlier part of it may amuse you." His hope was fulfilled and further amusement may be had from some of the earlier forms of adulteration recorded by Mitchell in Part II of the book.

Dyer was the oldest surviving member of the Society and he gives an account of its formation following a meeting of Public Analysts on August 7th, 1874. This meeting was called by Charles Heisch and G. W. Wigner and was presided over by Dr. Theophilus Redwood, and the list of those present contains many well-known names. The need of such an Analytical Society was evident, as it had to assume the duty of formulating standards of purity for foods and drugs liable to form subjects for prosecution of traders under the Acts of 1860 and 1872 dealing with adulteration.

An organising committee was appointed and submitted a report presented to a meeting on December 1st, 1874, at which seventeen public analysts were present. A President (Redwood), Vice-Presidents (Hassall and Wanklyn) and a Council were elected and, the great majority of the public analysts in the country having sent in their names as original or joining members, the Society of Public Analysts was fairly launched.

The first regular General Meeting was held on February 5th, 1875, and Dyer began his association with the Society. Dyer gives the following account:

> "The first members thus regularly elected by ballot were Professor John Attfield (Sir) William Crookes, C. W. Heaton, and W. C. Young. The election is also recorded of four associates among whose names that of the writer is recorded, a little incident which was kindly recalled from our first minute book by our Past President, Mr. Rudd Thompson, in his second annual address. At that time the writer enjoyed the good fortune of being

an assistant to the late Dr. Augustus Voelcker, and, being in this embryo condition, was eligible only for the associateship and not for full membership, to which however—if he may be pardoned for this further personal reference—he was duly promoted in the following year."

Dyer was elected to the Council in 1880 "at a very youthful age," in company with Hehner, who was not much his senior. The two friends became joint Honorary Secretaries in 1883 and Dyer was elected President in 1897 having been Secretary for fourteen years. Dyer's work for the Society was continuous, and only this year he had been nominated again as a Past President serving on the Council to be elected on March 5th. His service as a member of the Publication Committee of THE ANALYST was continuous also and the absence of his name on the cover will appear strange and call to mind our loss.

An extended review of the numerous papers published from Dyer's Laboratory would be out of place but a rather rough division may be made between those dealing with materials intended for human consumption and others of essentially agricultural interest. Lacking expert knowledge, I feel very diffident in making any appraisal of Dyer's work and hope I may be excused for any shortcomings in selection of examples.

As a Public Analyst for so many counties and boroughs he had at Great Tower Street necessarily to deal with an extensive range of food problems. Allusion has been made to the prevalence of adulteration—often very crude—about the middle of last century. But the purchaser may be prejudiced not only by the addition of foreign matter to an article but also by the abstraction of some constituent on which its nature depends. An abuse of this sort was the sale of partly exhausted ginger such as that which had already been used in the brewing of ginger beer. Dyer and Gilbard (ANALYST, 1893, **18**, 197) gave the composition of genuine and spent samples, determined the alcoholic extract of the residue obtained by evaporating the ethereal extract, whilst the amount of ash soluble in water also proved useful. Subsequent work on washed ginger was published in THE ANALYST (1899, **24**, 169). Dyer and Gilbard (*Ibid.*, 1896, **21**, 207) also turned their attention to "drawn" caraways which can be identified by their content of volatile essential oil and fixed ethereal extract. These random examples illustrate one type of work from the Dyer laboratory. More general interest attaches to papers on plant nutrition and agriculture generally.

It is probable that Dyer's continuous work on agricultural problems resulted from his early experiences in Voelcker's laboratory. Augustus Voelcker was consulting chemist to the Royal Agricultural Society of England and at his death was succeeded by his son John Augustus Voelcker who with his brother E. W. Voelcker were close friends of Dyer.

Dyer was always in close touch with the Rothamsted station and it was Dr. (Sir J. H.) Gilbert who directed his attention to the availability of "mineral" plant food in soils. There seemed to be fairly general agreement that phosphates were rendered soluble by organic acids in the root hairs of plants and it was a question how this acidity could be imitated *in vitro*. Both Tollens and Stutzer advocated 1 per cent. citric acid solution but the basis for this assumption needed experimental confirmation.

The assumption was tested and Dyer showed in an exhaustive paper that 1 per cent. citric acid solution was not far from the sap acidity (average 0·8540) found in the roots of plants. The roots of no less than 100 plants belonging to 20 different natural orders were examined (*Trans. Chem. Soc.*, 1894, **65**, 115–167). This paper contributed largely to Dyer's reputation and is well worth reading more than fifty years after its appearance, on account of the technique employed as well as for the results obtained. Further work connected with the Rothamsted station was published in the *Transactions* of the Royal Society.

Dyer served on many councils and committees and was at the time of his death still one of the "other persons" who, with their academic colleagues, form the Board of Studies in Chemistry of London University. His success as a chemist was largely due to the accuracy of his work and the habit of clear thinking. This proverbial accuracy led to a case—unique in my experience—where, the composition of a mixture set in a University examination being in dispute, samples were sent to Dyer and his results accepted. Added to this, he had a large fund of general information which made him an excellent companion and his kindly and sociable habits contributed to his success as a man.

We shall all, especially the elder members, miss his kindly presence and some of us have cause to remember with gratitude the sympathy he gave them in times of personal bereavement.

J. T. HEWITT

The Micro-Analytical Test for Purity in Food with Special Reference to Cereals

By D. W. KENT-JONES, A. J. AMOS, P. S. ELIAS, R. C. A. BRADSHAW and G. B. THACKRAY

(*Read at the Meeting of the Society on February 4th*, 1948)

Introduction

The examination of food, by what is known in the United States as a micro-analytical technique, for the presence of extraneous matter has, in recent years, seriously occupied the attention of the Food and Drug Administration in that country. It is now common practice in the United States for such tests to be made daily in the laboratories of mills, bakeries, confectioners and biscuit and cake manufacturers since, if a high count for extraneous dirt is found in food, prosecutions may follow. This test is commonly known as the "Filth Test," and it is not applied only to the examination of cereal products. Indeed, even in baked goods, there is evidence that many of the other ingredients are more impure than the cereal portion. At this stage our main experience, however, has been with cereals, so this paper deals essentially with the analytical procedure in determining extraneous matter (filth) in these products. Unfortunately, such extraneous dirt may also be a significant factor in most other foods, such as spices, chocolate, milk, meat products and fruit. The micro-analytical test should, therefore, be capable of being universally applied to foods although the technique employed must vary according to the nature of the food.

The technique of this micro-analytical procedure is admirably dealt with in the U.S. Food and Drug Administration Circular No. 1,[1] and considerable space is devoted to the matter in the last (sixth) edition of Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists.[2] For tests on cereals, attention is also drawn to the Report of the New York Section of the American Association of Cereal Chemists.[3] There can be, of course, many types of extraneous matter, such as grit, floor sweepings, earthy matter, excreta (especially rodent excreta), but, in general, the micro-analytical test as it is understood to-day is mainly directed to the determination of rodent hairs and of insect, mould and other fragments. If rodent hairs are found, this is *prima facie* evidence that there is also likely to be contamination with excreta, even though direct evidence of this is often harder to find. Rodent faeces always contain a mass of rodent hair, and wheat is occasionally contaminated with such rodent excreta, which are not easily separated from the grain and which, when ground up in the rolls, cause the presence of rodent hairs in the flour. Two small pellets of dry rodent faeces (weighing together 20 mg.) contained nearly 100 rodent hairs. The rodent hair may be regarded in the same way as *B. coli* in potable water, that is to say, not so much harmful in itself, but presumptive evidence of undesirable uncleanliness. If solid excreta are present in what may be regarded as an appreciable quantity, they can usually be separated by shaking the powdered, finely-crumbled product with a liquid of sp.gr. about 1·49 in a separating funnel, which permits the ground cereal to float and the excreta to fall.

No definite standards are set in the United States for such extraneous matter, *i.e.*, for the number of rodent hairs or insect fragments per 100 g. of material. Food should be essentially free from extraneous material; if it is not, warnings are issued and, in bad cases, prosecutions undertaken. Cleanliness in manufacture and the taking of precautions, consequent upon the findings of those dealing with the examination of dirt in food, have undoubtedly resulted in cleaner food. While there is no direct evidence of harm to health from the presence of such matter in food, yet all will agree that, if food can be made cleaner and under more hygienic conditions, this should certainly be done. There is, of course, a limit to the implications of the test and they should not be pushed to extremes, particularly in view of the inherent difficulties of the method.

The so-called micro-analytical test comprises two distinct steps. First, the dirt and extraneous matter have to be separated from the food, and secondly, they have to be recognised and counted, and for this second step it is generally necessary to employ a microscopic technique. In this paper we give the results of our experiences in this field after many

months of work, and we gratefully acknowledge the initial help we received from many friends in the United States, who allowed some of us to see the test in operation in the first place. Different laboratories there have slightly different techniques. We have examined many of these and give what we consider to be improved procedures. The test, as described, can be carried out in any ordinary food laboratory and, although it is desirable to employ, purely for ease of operation, certain attachments in using the microscope, these are not essential. They only render recognition of extraneous matter easier, make the work less laborious and assist in obtaining better agreement on counts.

Separation of extraneous matter and filtration

The food must be partially digested *in vitro*, so that the extraneous matter can be separated, but the digestion procedure employed must be one that rodent hairs, insect fragments, such as portions of mites (tyroglyphids), weevil and meal worms, and even mould fragments can withstand without losing their distinctive microscopic features. Strong alkali, which destroys hair, must be avoided. Starch must be hydrolysed and protein broken down by enzymic digestion. The actual separation, which follows the digestion, is normally done by shaking up the digested food with a light mineral oil, such as petrol. The oil preferentially wets the rodent hairs, insect fragments, etc., which then float up and congregate at the oil/water and oil/glass interfacial layers. The bulk of the lower layer containing the food (once all the extraneous matter has been removed from it, and for this more than one extraction with the mineral oil is necessary) is discarded and the dirt collected by filtering the petrol and the residual interfacial layer through a ruled filter paper on a Buchner funnel. Other procedures and variations are discussed later.

The question of sampling is an important one. For convenience of working we have used in routine tests 25 g. of the foodstuff and, if this is a baked product, it has to be remembered that, in making, this receives a good mixing in the dough stage. In the United States, often 100 g. of material or more are used, but obviously steps should be taken to ensure, as far as is possible, that the sample represents a fair average of the food being tested. In important "border line" cases a larger quantity than 25 g. is necessary, and the test should be made in duplicate or triplicate.

Before beginning the food digestion, some preliminary fat extraction is desirable except for such foods as flour, where the fat content is low, for example, below 2 to 3 per cent. As the solvent will "wet" the rodent hairs, precautions must be taken to see that no extraneous matter is lost at this stage. A useful way to effect this is to tie the sample in a filter paper bag. When the defatted material is subsequently removed, the filter paper should be washed down with solvent or alcohol and these washings evaporated in the beaker used for the digestion.

Several procedures have been advocated for the digestion of cereal foods. The earlier recommendations using salt and not digesting the food are not satisfactory, and result in inaccurate and low counts. In one digestion method the cereal is mixed with excess of water (say, up to 250 or 350 ml. for 25 g.), boiled to gelatinise the starch and cooled to about 35° to 45° C.; 0·5 to 1·0 g. of pancreatin is sprinkled on and the digestion carried out at this temperature for some 3 to 6 hours, or even longer. In another digestion method, 400 ml. of dilute hydrochloric acid are added to the cereal food and the mixture is boiled in presence of a light mineral oil. After 15 to 20 minutes boiling, the mixture is cooled to room temperature and the extraneous matter removed from the interfacial layer.

From the results of our experiments we prefer a third method, which is based on that given by the A.O.A.C.[2] and is essentially a combination of the two methods just described. It is given in detail later. This method, which involves both boiling with acid and digestion with pancreatin, is preferred, as the digested food is in a less viscous state, so that the subsequent extraction with petrol is easier, emulsions are less likely to be formed, and the final counting operation is facilitated. We have carried out tests on the same flour (85 per cent. extraction) by the three methods. Low counts result from the first method (use of pancreatin only) and, although there is reasonable agreement between the second method (acid boiling and no pancreatin) and the method we suggest, we prefer the latter for the reasons stated.

With respect to apparatus, two types are in use for extracting the digested food with petrol or light oil. There is the apparatus known as the Wildman trap, illustrated in Fig. 1. This consists of a conical flask (say, about 1 litre capacity) containing on a brass rod of approximately 3/16 inch diameter a rubber bung which, when pulled up, fits into the neck

of the flask. The rod, threaded at the end, carries a nut and washer fastening the bung. The nut should be countersunk to prevent breakage of the flask during use. The amount of liquid used is such that when the bung is pulled up by the rod into the neck of the flask, it is possible to pour off for filtering the supernatant oil and the interfacial filth layer without interference from the bulk of the liquid containing the digested food. This apparatus is particularly applicable to coarse materials, such as dried fruits, whole wheat, and the like.

For the examination of ground cereal products we prefer the alternative method in which special separating funnels are used—a procedure which we believe is gaining ground in America. These separating funnels, which are shown in Fig. 2, should have a capacity of about 600 ml., or larger if a quantity of more than 25 g. of material is taken. The usual stopcock is removed and replaced by a rubber tube of diameter about 9 mm., which can be closed with a strong screw clip. The rubber exit tube should be renewed fairly frequently, as otherwise minute cracks may develop on the inner surface and retain hairs.

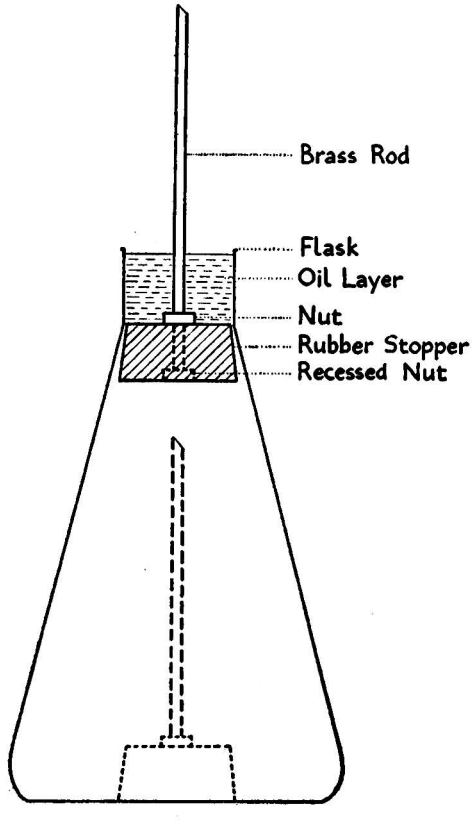


Fig. 1. Wildman Trap.

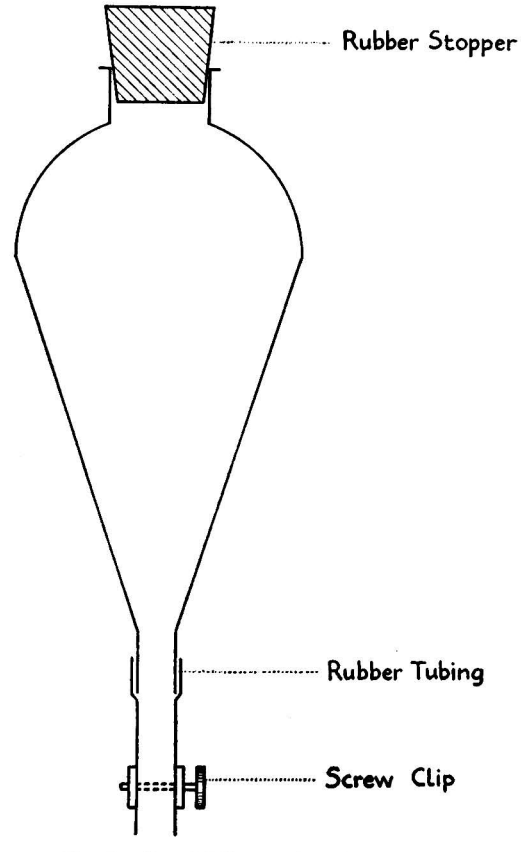


Fig. 2. Special Separating Funnel.

It is the usual practice in the United States to filter the interfacial layer, etc., on a smooth filter paper and we have found that the smooth side of a No. 1 Whatman paper is suitable. The paper can be ruled horizontally with pencil lines. The distance between the ruled lines depends on the magnification being used, and it is convenient to rule so that the distance between two consecutive lines can be covered by two fields of view. With the magnifications we use normally this width is about 6 mm. If this is done, it is also helpful to have some vertical lines so that the paper can be mapped out and suspected hairs or insect fragments easily re-found when necessary for further examination.

The paper is examined wet, and if the count is not carried out immediately it should be kept covered, for example, in a Petri dish, so that no dirt is lost and no dirt falls on it.

Details of the complete procedure that we finally adopted as the most convenient and the most satisfactory for the extraction and collection of extraneous matter are as follows:—

METHOD—

Weigh 25 g. of the material, de-fat if necessary, and put into a 400-ml. beaker. Boil 100 ml. of 0·5 *N* hydrochloric acid in a separate beaker, add the boiling acid quickly to the material and stir into a paste thoroughly for 30 seconds before placing the 400-ml. beaker over a small flame. Avoid the presence of unwetted material on the bottom of the beaker; any suitable procedure to effect this will suffice. If the paste seems too thick, dilute somewhat with hot water. Boil the mixture for 10 minutes, cool and dilute with about 100 ml. of distilled water. Add about 9·5 ml. of 5 *N* sodium hydroxide, stirring to avoid local concentration; add 2·5 ml. of saturated trisodium phosphate solution and adjust the *p*H to 7·0, using phenol red (0·2 per cent. aqueous solution) as external indicator, by adding a few drops of acid or alkali as necessary. When the temperature falls below 40° C., add 1 g. of pancreatin, which should be free from any contamination, suspended in 20 ml. of water. Dilute to about 350 ml., mix thoroughly and incubate at about 37° C. overnight.

Pour the digest into a special separating funnel of about 600-ml. capacity prepared by cutting off the tap and replacing it by a wide rubber tube with screw clip. Add 25 ml. of petrol. Shake gently to distribute the petrol throughout the solution. Allow to separate for 20 to 30 minutes. Run off the bulk of the digest into the original beaker, but leave sufficient to form a small layer under the interface. Keep the removed digest for a second separation. Add to the layers in the funnel about 400 ml. of distilled water. Mix gently by swirling and allow to separate. Draw off and reject the washings and add a further quantity of distilled water. Mix, allow to separate, and draw off most of this second washing. Run the liquids remaining in the funnel through ruled filter paper on a Buchner funnel, or collect by one of the alternative methods described later. In the filter paper technique the paper should rest upon a light layer of kieselguhr to avoid the debris congregating over the holes and the paper should be large enough to extend some distance up the sides of the funnel. Replace the original digest in the funnel and extract again with petrol as before. Remove the bulk of the digest and then wash the petrol and the small volume of digest underlying the interfacial layer twice with distilled water as previously described. Reject the washings and collect as before. Wash down thoroughly the inner surface of the separating funnel and of the rubber outlet tube with alcohol from a wash bottle and finally with distilled water. In view of the firmness with which hairs tend to adhere to the glass, the addition of a few drops of a wetting agent, such as Teepol, to this final water wash is advised. Collect any extraneous matter in these washes. Serious errors can arise through not properly washing out the glass apparatus and leaving hairs on the glass ware.

Procedures for examining microscopically the extraneous matter collected on the ruled filter paper, or by other means, are described later.

Report the results as the number of specified contaminants, *e.g.*, rodent hairs or insect fragments, etc., per 100 g. of sample or, as is now customary in the United States, per pound.

Although filtering the collected extraneous matter through paper, as described, has advantages, an important one of which is that it imposes no restriction on the volume of liquid employed to detach and wash the extraneous matter, yet there are also advantages in running the petrol - water mixture direct on to a ruled glass surface from which it is evaporated. Methods using the latter procedure make easier the subsequent microscopic examination. Two such methods that we have employed are given below.

(1) Allow the washed petrol extracts, together with the interfacial layer and a small amount of the aqueous layer, to fall drop by drop on an inclined ruled glass slide fixed at approximately 10° to the horizontal. For convenience, this slide should be of the width of a microscope slide, but twice to three times as long. At a point 4 inches from the lower end it is just cleared by a microscope slide held at an angle of approximately 10° to 15° to it. The liquid dropping down the long glass slide is spread between the two glass surfaces into a wedge-shaped film approximately 1 cm. long. The long slide is supported clear of a suitable heater covered with

asbestos, so that when the liquid flows slowly down the glass evaporation takes place and it is finally held as the wedge-shaped film until evaporation is complete. This is most successfully accomplished if a thermometer resting on the microscope slide registers 50° to 60° C., according to the liquid being evaporated.

(2) Allow the washed petrol extracts, together with the interfacial layer and a small amount of the aqueous layer, to evaporate on a water-bath in a Petri dish, suitably ruled. Ensure that at any one time there is not much liquid in the dish. This prevents hairs, etc., climbing the sides. Rinse out the separating funnel and rubber exit, first with 20 ml. of alcohol and secondly with 20 ml. of water containing a few drops of Teepol. Evaporate these under the usual conditions in the same Petri dish. Ensure by suitable manipulation that the debris is evenly distributed over the centre of the dish and away from the edges; this requires washing the edges in the final stage with light petroleum. Just cover the deposit with about 1 ml. of a 3 : 1 mixture of castor oil and alcohol.

With some coarsely ground cereals, such as oatmeal or wheatmeal, difficulties are encountered because branny particles tend to collect in the interfacial layer and render

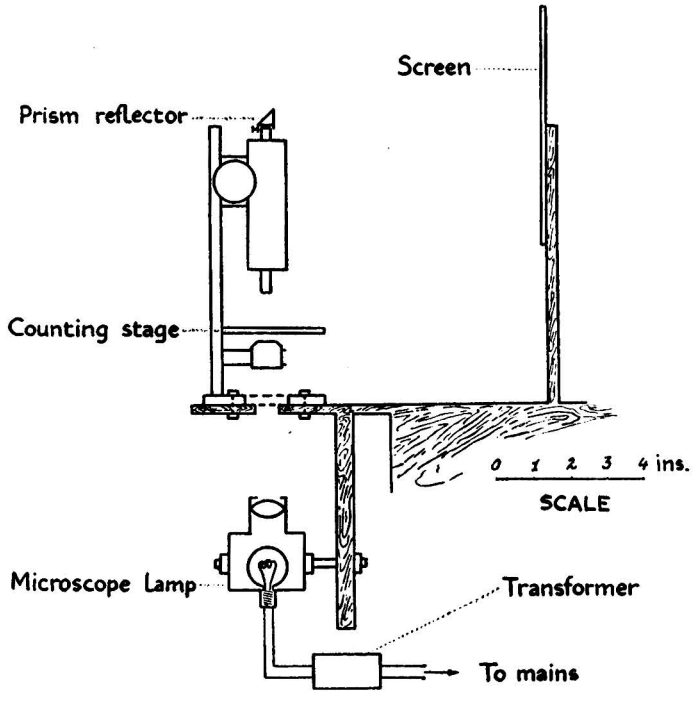


Fig. 3. Suitable arrangement for projection method of making counts.

difficult the subsequent microscopical examination. We have tried various procedures to minimise the interfering effects of bran particles by adjustment of the time of digestion and the use of 40 per cent. alcohol in the shaking out, but have had little success. In such instances it is advisable to spread the debris over a larger surface when examining under the microscope.

Microscopic examination and count

The collected extraneous matter can be examined microscopically in the following ways and the appearance of the dirt is influenced by the means employed.

(1) Viewed by *reflected* light from the filter paper, as is the normal practice in the United States.

(2) Viewed by *transmitted* light either through the filter paper oiled with castor oil, for example, to make it translucent, or through a ruled glass surface direct.

(3) As in (2), but throwing the magnified image on a suitable screen by means of such an arrangement as is described later.

It is necessary to be conversant with the appearance of the most common types of extraneous matter likely to be encountered, and on this matter considerable valuable information will be found in the Food and Drug Circular No. 1,[1] already mentioned, especially with reference to insect fragments. Another useful reference book is that issued by the Ministry of Food, entitled "*Insect Pests of Food.*"[4] The question of hairs is dealt with later in this paper, but it has not been possible to deal in similar detail with insect fragments.

In the United States it is customary to rely entirely on viewing the ruled filter paper, on which the dirt is collected, by means of reflected light. This procedure is sound, but the counting is often tedious, each filter paper often taking 2 or 3 hours. It is equally as simple to use transmitted light, which we in fact prefer. The filter paper is allowed to dry naturally and then treated with just as much oil as it will absorb. Castor oil diluted with 25 per cent. of alcohol is a convenient medium, but paraffin is also satisfactory. The paper is placed between two glass plates, pressed, and examined by transmitted light.

The separated and collected extraneous matter is examined microscopically and counted, normally at a magnification of 35 to 70. Any ordinary microscope will suffice, although the modern binocular type, such as the Greenough, is very suitable as it involves less eye-strain. We have found it convenient to work at a magnification of about 50 (although 35 would suffice) and a field of view of about 3 mm. With an ordinary microscope this is obtained with a 1-inch objective and a × 8 eyepiece.

A convenient arrangement is shown in Fig. 3. This consists of a special projection lamp, such as "Cosmos 55," 6 volts 5 amps., together with a lens to focus the beam on the iris diaphragm of the microscope at a distance of about 9 inches. A projection lamp can be bought with transformer, case and lens complete.

With this arrangement it is possible to throw the image on a screen by means of a prism fixed to the eyepiece. We recommend placing the screen, which should have a glossy smooth surface—we use art paper—about 15 inches from the microscope which, with the 1-inch objective and × 15 eyepiece, gives a picture about 10 inches in diameter. The magnification on the screen is about 130 to 150 and, under these conditions, the appearance of the hairs, etc., is rather different from that as seen direct in the microscope. The magnification is greater, but the clarity is reduced. There is considerably less strain on the eye with this arrangement, but it may be necessary to verify doubtful hairs and other objects by taking off the prism and looking (through a dark glass) direct in the microscope. If the filter paper procedure is not adopted, but a method involving evaporation direct on a glass surface, the microscopic examination, either direct or particularly via the screen, is much easier.

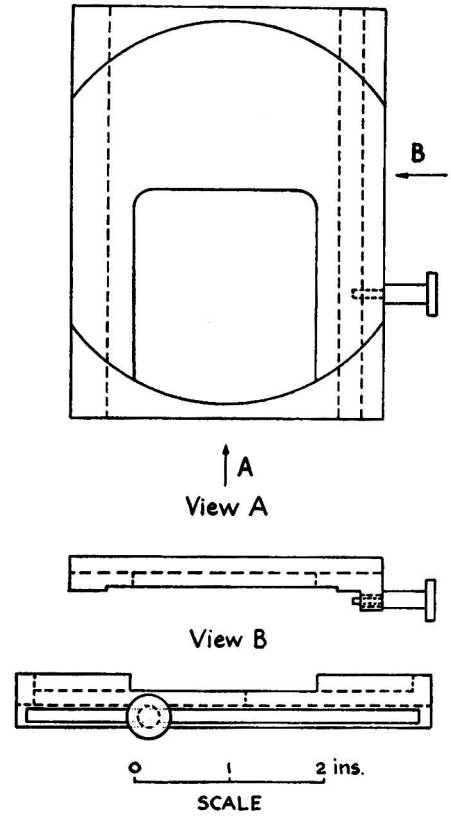


Fig. 4. Mechanical stage suitable for counting procedures using Petri dish or glass plate.

Counts can be made by moving the ruled paper or glass by hand. This, however, is tedious and difficulties arise in ensuring that a portion of the field is not overlooked or counted more than once. Hence, some sort of mechanical stage is desirable. Such a device is shown in Fig. 4, and with this arrangement the dish should be ruled in concentric circles. The stage is essentially a brass plate $3\frac{1}{2} \times 4\frac{1}{2} \times \frac{1}{4}$ inches, which rests on the table of the microscope. The plate has a rim $\frac{1}{2}$ inch deep which slides against the side of the microscope table. In the rim is a groove, through which passes a lock-nut. Cut in the brass plate is a circular trough, in which the glass dish just fits. A portion of the brass plate is cut away to allow

the light to pass. The dish just protrudes sufficiently to be turned by the finger, thus enabling the plate to be revolved, and hence all of it to be viewed with a minimum of trouble.

An alternative stage consists of a smooth aluminium platform, 6 × 9 inches, bolted to the microscope through the holes that normally hold the slide grips, with another smooth aluminium plate, 4½ × 6 inches, sliding on this. Two pieces of wood about ½ inch thick are screwed down on each side of the sliding aluminium plate, and the Petri dish, or glass plate, just fits between them. The dish can thus be moved up and down each ruled line to permit convenient counting. The sliding plate has a piece of wood screwed across the top, which fits underneath the aluminium platform, thus acting as a guide and enabling linear traverse to be made. If a microscope with a stage having a good traverse in both directions is available, there is no necessity to make a special stage for counting the glass slide or the horizontally ruled filter paper.

Each analyst will use whatever technique appeals to him, but we recommend direct evaporation on glass and the examination of the deposit by transmitted light, throwing the image on a screen. Under these conditions the count can be made in 40 to 60 minutes.

It is important for the analyst who is new to this test to know on what to concentrate, and we have felt it desirable to simplify the matter in the following way, even if the proposed classification is not perfect. Even then different operatives may get somewhat different results, especially in differentiating rodent hairs from other hairs and in the insect fragment counts.

(1) The count should be reported as:—
   (*a*) Number of rodent hairs.
   (*b*) Number of other hairs.
   (*c*) Number of insect fragments.
   (*d*) Number of mould fragments, etc.

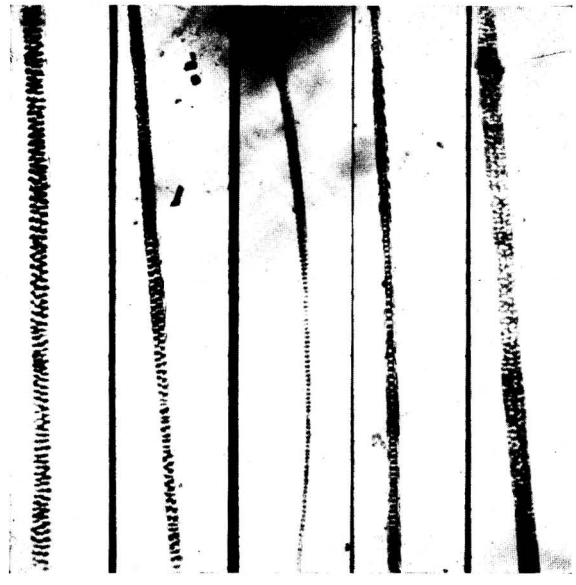
(2) Since the most important factor is the number of rodent hairs reported, only absolutely typical rodent hairs should be reported as such. This may mean that a few less typical rodent hairs may be missed or reported under the heading of other hairs but, except in bad cases, the count of the other hairs is not regarded as serious. It is essentially the typical rodent hairs that indicate contamination with rodent faeces. The rodent hairs regarded as typical—containing striated medulla—are shown in Figs. 5 and 6, and they probably represent 90 per cent. or more of the total rodent hairs. We have come to this conclusion after examining ground-up rodent faeces (which always contain a mass of rodent hairs) and hair from different body-parts of numerous types of rats and mice.

(3) Vegetable fibres, such as the hair from cereal products shown in Fig. 11, are not reported.

(4) Difficulty is encountered with insect fragments, and only those reasonably easily recognisable should be reported. It is true that a very prolonged examination of certain doubtful cases may increase the insect fragment count but, as previously stated, there is less objection to insect fragments except when the count is exceptionally high. In normal working we select for further examination only those fragments that do not show the colour and structure distinctive of the material under test. These can then be examined for confirmatory evidence, such as shape and outline, internal structure (as in larvae), or a covering of minute hairs. If any evidence of this kind is present the fragment is counted (a procedure to intensify the colour of insect fragments has been set out in the journal of the Association of Official Agricultural Chemists[5]). A high insect count is an indication that the mill requires a thorough cleaning out and probably fumigation.

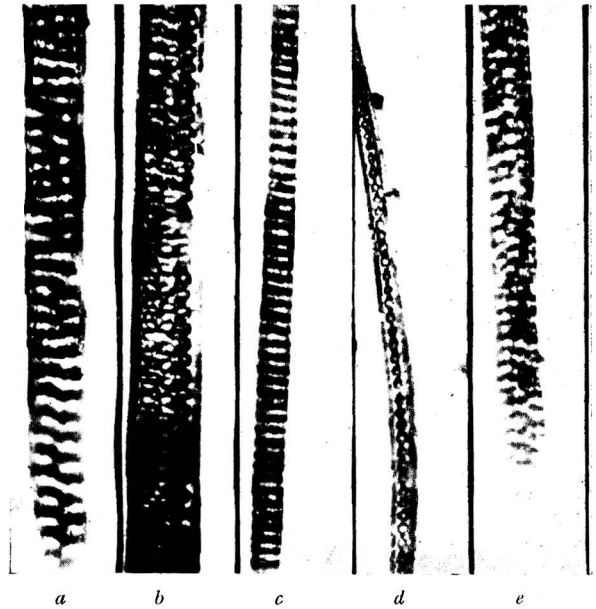
(5) A close watch should be kept for mould fragments as an indication of unsoundness of the food.

Bearing these facts in mind, we feel it necessary to be able to recognise not only typical rodent hairs (there being no obvious difference between rat and mouse hairs, except perhaps in size), but also human hair of various colours, cat and dog hairs, vegetable fibres, cereal hairs and the more obvious insect and mould fragments. These are shown in Figs. 7 to 13. The lower magnifications, and this applies also to Figs. 5 and 6, are as seen down the microscope,



a *b* *c* *d* *e*

Fig. 5. Characteristic rodent hairs. Rat hairs *a*, *b*, *c*, *d*, and mouse hair *e* at a magnification of 60 diameters.

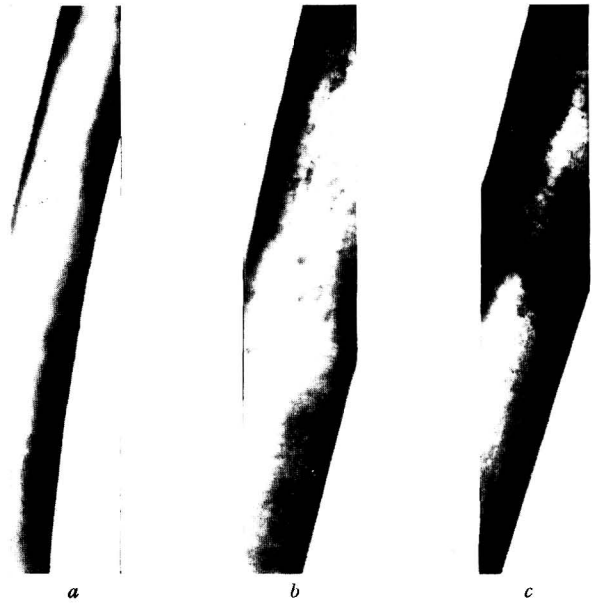


a *b* *c* *d* *e*

Fig. 6. Rodent hairs as in Fig. 5 but at a magnification of 150 diameters.

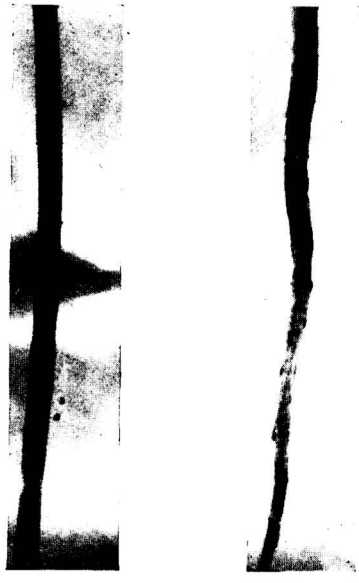
a *b* *c*

Fig. 7. Human hairs at a magnification of 60 diameters (*a*, blonde; *b*, red; *c*, brunette).



a *b* *c*

Fig. 8. Human hairs as in Fig. 7 at a magnification of 150 diameters.



a *b*

Fig. 9. Animal hairs at a magnification of 60 diameters. *a*, dog; *b*, cat.

a *b*

Fig. 10. Animal hairs as in Fig. 9 at a magnification of 150 diameters.

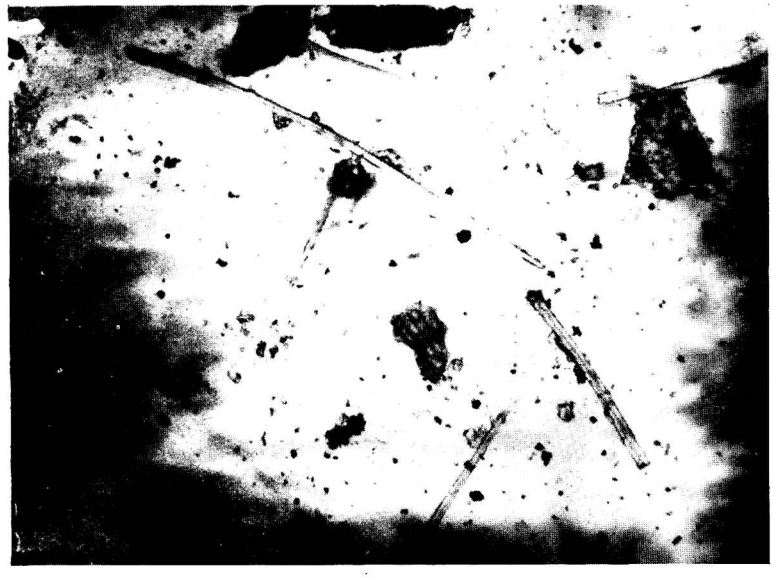


Fig. 11. A typical field as obtained from flour, showing wheat hairs and bran at a magnification of 60 diameters.

Fig. 12. Insect fragments at a magnification of 60 diameters.

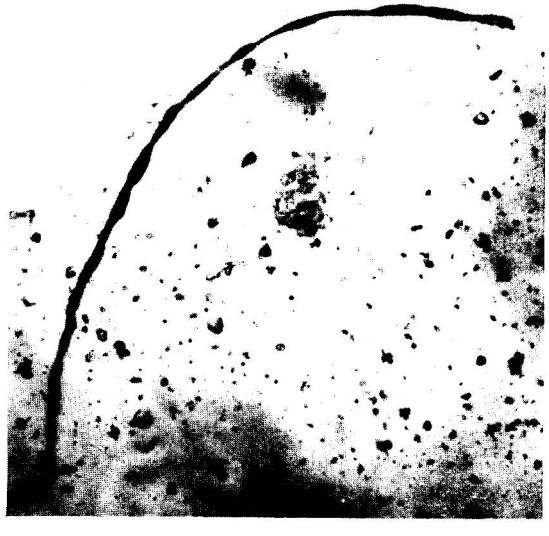


Fig. 13. Fibre at a magnification of 60 diameters.

and the higher magnifications are as seen on the screen. (All the photographs shown were made after evaporation on glass and not after using the filter paper technique.)

There is no difficulty in differentiating between rodent hairs and human hairs. The photographs of animal hairs given in this paper, however, need a little qualification to avoid misinterpretation. Some cat hairs under high illumination do show striations in the medulla. The cortex or outside portions of the hair, however, contain so much pigment that the striations do not persist when the illumination is reduced by means of the iris diaphragm. When viewed by reflected light or projected on the screen the illumination is automatically lower; the cat hairs, therefore, appear completely black, as shown in the photograph. Some dog hairs have a medulla similar to that shown in Fig. 6 (*d*), but all the dog hairs we have seen have a distinct band of black pigment along each edge which is absent in the rodent hair. For ultimate diagnosis the reader is referred to Food and Drug Circular No. 1,[1] but for most purposes the above rules suffice.

Results obtained

First an effort was made to obtain some idea of the recoveries that might be expected when a known number of rodent hairs were added to flour. These results are shown in Table I and indicate that, considering all the difficulties involved, the test is satisfactory for the information required.

Table I

Recovery results

		Petri dish procedure		Oiled filter paper procedure	
		No. of hairs recovered	Percentage recovery	No. of hairs recovered	Percentage recovery
Original flour		0	—	0	—
No. of rodent hairs added per 100 g.					
Long hairs (30 mm.)	16	16	100	20	125
	80	80	100	72	90
Short hairs (1 mm.)	16	20	125	16	100
	80	78	97·5	84	105

It has been suggested that it is difficult to recover in baked goods the exact number of hairs known to be present in the ingredients. Much depends on the digestion method employed but, so far, we have not been able to make enough experiments on this point to speak with confidence on this aspect of the problem.

Table II gives some results of applying this test to cereal products. The table gives an idea not only of the results obtained, but also of the agreement between different operators, and other factors. It must be remembered that the question of sampling has to be borne in mind and also that the figures given are the result of multiplication by four, since only 25 g. are used in the actual test.

A selection of non-cereal products was also examined. The results are summarised in Table III. It was not found possible to use the method given in this paper for all these products. The currants, for example, left much skin at the interfacial layer, even after repeated washing. This made counting difficult, and therefore the figures given are on the low side. With the prunes, on the other hand, the method was quite satisfactory and needed no modification.

With regard to chocolate and spices, our work has confirmed the conclusion reached by the Committee of the New York Section on Procedures for the Examination of Food Products for Extraneous Materials (1947)[6] that the general methods used for cereals are not satisfactory for this type of product. We have, therefore, used the method described in that report. This consists essentially of heating the material under reflux, together with dilute hydrochloric acid, acetone and light mineral oil, followed by a separation similar to our own, except that shaking to mix the two layers is unnecessary and should be avoided. We do not propose to deal in detail with the application of this test to non-cereal products, our present impressions being that the divergence between the results of different operators may be greater than that now likely to be obtained with cereal products if the method used in this paper is followed. Further work, however, may well effect an improvement in this situation.

TABLE II

EXTRANEOUS MATTER (DIRT) CONTAMINATION OF CEREAL PRODUCTS

All results reported are per 100 grams of product examined

Sample	Rodent hairs	Other hairs	Insect fragments
Imported Canadian flour (white)	0	0	0
Duplicate—same operator	8	0	0
Imported Australian flour (white)	8	0	0
Duplicate—same operator	12	0	0
A series of imported American flours (all white)	0	0	0
	4	32	4
	8	4	12
	0	4	8
Home-milled biscuit flour (white)	4	0	0
Duplicate—same operator	4	0	0
Home-milled biscuit flour (85 per cent. extraction)	4	4	4
Duplicate—another operator	12	0	0
A series of home-milled flours (all 85 per cent. extraction)	0	28	16
	4	(many)	4
	4	12	0
	0	0	40
	72	16	0
	4	0	36
	16	0	44
	8	24	32
	8	(many)	8
Two home-milled flours (85 per cent. extraction)	0	0	8
	2	8	2
(First figure in each case our own. Note the other lab. used 50-g. samples.)	16	0	16
	8	4	0
Two flours from New Crop (1947) wheat	4	12	4
	0	—	—
(First figure in each case our own. Note the other lab. has reported only the rodent hair count.)	4	24	12
	0	—	—
Two flours from Old Crop (1946) wheat	24	16	20
	40	—	—
(First figure in each case our own. Note the other lab. has reported only the rodent hair count.)	4	16	8
	12	—	—
Wholemeal	150	0	16
Oatmeal	120	0	0
Bread	4	32	0
Breakfast foods (flakes)	48	0	8
Biscuits (brown type, including a meal ingredient) two samples	24	0	16
	40	0	12
Biscuits (butter)	24	16	0
Christmas pudding (farinaceous portion)	16	0	8
(fruit portion)	12	0	4

TABLE III

EXTRANEOUS MATTER (DIRT) CONTAMINATION OF NON-CEREAL PRODUCTS

All results reported are per 100 grams of product examined

Sample	Rodent hairs	Other hairs	Insect fragments
Currants	0	4	20
Prunes	0	0	16
Ground mixed spices	12	24	108
Duplicate—another operator	0	50	90
Chocolate	12	24	4
Duplicate—another operator	0	24	0

GENERAL OBSERVATIONS

This paper is mainly concerned with indicating an analytical technique to deal with the determination of extraneous matter (filth) in cereal products. Procedures have been described which should enable the analyst to obtain reasonably reliable results. It may be desirable, however, to indicate how improvements in the cleanliness of cereal products could be brought about. It has been admitted that, in baked goods, often the factor responsible for a high count is not the cereal but the other ingredients, but it must be remembered that usually these other ingredients are used in smaller proportion than the flour. Yet sometimes even flour has a higher count than is desirable and possibly a higher contamination than is usual in the United States, where recent improvements in purity have taken place since the micro-analytical tests have been instituted. It must not be assumed from these observations that flour milled in Great Britain is not normally of high purity. Compared with other foods it is good, although milling to long extraction aggravates the position, particularly as the extraction of 85 per cent. has to be obtained on dirty wheat and this means that millers are reluctant to remove as much screenings (including rodent dung) from wheat as was formerly usual. In fact, if this test is to be applied and a new standard of purity insisted upon, there is a clear case for a revision of the method of calculation of the extraction from a dirty wheat basis to a clean wheat basis. Naturally this would necessitate a limit to the amount of screenings that it would be permissible to extract.

The British miller, as well as those engaged in the manufacture of cereal products, is a skilled and conscientious manufacturer, but special care in rat and mice proofing is desirable, as well as constant attention to cleanliness generally, including that of sacks. It is our view that most of the trouble comes from the presence of rodent faeces (and particularly mice faeces) in the wheat; these are not easily removed unless special steps are taken and it is not always easy to do this. The screen room of a mill is largely designed to remove impurities from the wheat, prior to the grinding operation, the methods being based on differences in size and shape between wheat and the impurities. The difficulty is that the faeces vary so much in size and shape. Special procedures for removing dry faeces may be proposed, but probably much can be done by efficient scouring of the wheat, followed by strong aspiration. Flotation in the washing process may also help. If such steps are not taken, the count of rodent hairs may vary considerably from time to time according to the contamination of the grain with faeces. According to some determinations made on every fifth sack, results of which were kindly sent us by other workers in this field, white flour from certain reasonably clean new crop wheat gave, per 100 g., rodent hair counts of nil to 4, while the counts on the old crop, more highly contaminated with faeces, was 12 to 40, and averaged about 28.

On the whole, and in view of all the circumstances, our results suggest that generally the standard of purity of flour is reasonable, but capable of improvement. It has been suggested that the rodent hairs in the faeces become disintegrated in milling, so that a simple record of the number of hair fragments may be misleading. Our experience is that there is little substance in this view, since the average length of hairs in faeces and in flour is similar. We have attempted to make certain grinding experiments on mixtures of faecal pellets and wheat, measuring the length of hair fragments in both the carefully teased out original pellets and in the contaminated flour after grinding. Satisfactory control in such experiments is difficult, but the general results confirmed the view we have already expressed.

There is, however, a case to be made for the proposal to report not merely the number of hair fragments, but the total length of the hairs. This would not be difficult to do approximately as, judging from the extent to which it stretches across the field of view, the diameter of which is known, the worker knows the length of each fragment and hence the total length. The hair fragments vary from below 1 mm. to occasionally as high as 10 mm., but a little under 2 mm. would seem to be the *average* length of the majority of the hair fragments.

Summary

Improved methods, which include several differing techniques, for the examination of cereal foodstuffs for the presence of extraneous matter, are given, and photographs of hairs, etc., are shown to assist in identification of such matter. A procedure is advised for separating the extraneous dirt from the food (evaporation on glass is preferred to filtration), and an arrangement is shown by which the image of this dirt is thrown on a screen. This last step relieves eye-strain and makes generally for greater accuracy. Some results of applying the method are presented.

We gladly acknowledge the assistance we have had from many helpers and mention in particular Dr. J. B. M. Coppock, Director of the British Baking Industries' Research Association, and Mr. C. H. Groves, who was responsible for the photographs.

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88, Madeley Road
Ealing, London, W.5
and
British Baking Industries' Research Association
Chorleywood Lodge, Chorleywood, Herts.

Discussion

Dr. E. B. Hughes said that the Society was very much indebted to the authors for this valuable paper. Dr. Kent-Jones had presented the paper in an admirable way and had been very fair to the industries concerned with the problem. This added one further example to the many which had earned him his excellent reputation, and members would be very grateful to him.

Dr. J. B. M. Coppock expressed his pleasure that his colleague Mr. Bradshaw had been able to participate in this work and asked whether the authors could indicate what an average rodent hair count in flour would correspond to in terms of number of wheat grains per piece of rodent faeces.

Mr. R. W. Morris asked whether the test would give misleading results if applied to products, such as chocolate, that were subjected to severe grinding. Would not rodent hairs and insect fragments get ground up?

Mr. N. Heron described a modification of the American technique that was found to be satisfactory in a recent examination of biscuits for rodent hairs. The material at the interface was transferred to a No. 540 Whatman filter paper ruled with lines 5 mm. apart, and the paper and residue were washed once with alcohol. The paper was then transferred to a Petri dish containing a layer of chloral hydrate less than 1 mm. deep, and allowed to stand for about ½ hr., but not more than 2 hr., at room temperature. It was then examined by transmitted light, at a magnification of 25, with a binocular microscope. The light beam was focussed by a concave mirror, the source of light being a Pointolite lamp fitted with a condenser. The characteristic markings of rodent hairs were readily recognised, but any doubtful hairs were removed with fine forceps and examined at 150 diameters. Although chloral hydrate causes some swelling of animal hairs, there is not sufficient distortion under the conditions described above to prevent recognition of rodent hairs.

Miss E. I. Beeching asked to what extent the use of the Entoleter would destroy traces of animal or insect faeces or debris and interfere with the correctness of counts.

Mr. T. H. Fairbrother said he thought the Entoleter would cause some breaking up of the faeces, and it is necessary to have a complete sieving system put in immediately before the Entoleter.

Dr. N. L. KENT said that the use of the Entoleter on washed English wheat containing rodent excreta pellets caused slight breakage of the wheat with practically no break up of the rodent pellets.

Mr. F. C. HYMAS asked if it would not be possible, at least with flour, to concentrate the fragments on a smaller surface than that of a Petri dish and so reduce the tedium of counting.

Dr. J. H. HAMENCE asked whether, in view of the serious implication that might arise from the finding of "rat excreta in flour," it was possible to distinguish between rodent hairs that were excretory and those that might be introduced into flour otherwise, *e.g.*, owing to rats having rubbed themselves against flour bags. Furthermore, he asked if it was possible to detect the presence of mites' eggs in cereal products by the method described.

Mr. J. KING remarked that Dr. Kent-Jones, in his textbook had dealt adequately with the widely-differing bacterial counts in flours. Did any correlation exist between bacterial counts and rodent hair counts?

Mr. C. L. CLAREMONT asked if comparisons had been made of counts for cereal products from large and small producers, and if any attempt had been made to identify insect fragments, *e.g.*, whether due to *Tribolium* or *Ephestia*.

Mr. J. G. HAY asked if it was known whether loss of hair by rats was subject to any seasonal variation.

Dr. E. C. WOOD asked if Dr. Kent-Jones had any evidence as to the homogeneity of flour, such as would be obtained from counts on a dozen or more separate 25-g. samples of the same flour. In other words, was it not possible that occasional faecal aggregates or clumps of insect fragments might survive the process of milling and give rise to high counts, not truly representative of the batch, in odd single samples?

Dr. E. E. TURTLE drew attention to the importance of attempting to correlate with counts of fragments the general hygienic conditions in premises in which flour is produced. It was also most desirable to carry out bacteriological tests in conjunction with counts. He pointed out that in a technique involving digestion with pancreatin there was a possibility that insect fragments other than those containing chitin would be destroyed. Under certain conditions this would be important, because some insects at stages in their life cycles, *e.g.*, some larval stages, have only very small proportions of chitin. They might therefore be completely digested during the preparation for microscopic examination.

Mr. D. W. POVEY, speaking as one concerned with flour milling engineering, pointed out that although by basing the flour extraction on clean wheat, instead of according to present-day regulations, it would be possible for millers to remove a great deal of rodent excreta with existing available plant, a perfect separation would not be possible, because the physical properties at present employed as a basis of separation do not remain, in the case of rodent excreta, a constant factor. New plant and methods are, however, being devised, employing entirely new principles, by means of which it is hoped to effect a perfect separation, but this will take some time. It should be appreciated that at the present time, even with an extraction based on clean wheat, it would not be possible to produce a flour entirely free from rodent hairs. It is far better to remove rodent excreta in the whole state than to break them up and endeavour to remove the hairs; these attach themselves firmly to the bran skins and are most difficult to remove. This point is illustrated by the comparative high contamination of whole meal flour.

Professor E. S. HAWKINS drew attention to the special importance of contamination in oriental grain, rodents being a more dangerous scourge in the East than here.

Mr. E. G. RAYNES asked if the authors had any information as to the standards used by American authorities in rejecting foodstuffs exported from this country.

Mr. C. H. MANLEY mentioned that a year ago he examined a large tin of dried full-cream milk that the purchaser suspected of containing mouse dirt. About fifty dark particles about $\frac{1}{8}$ in. long were isolated from it. Some were single and some in pairs, but they were not dark enough in colour to be mouse dirt, nor did they contain undigested wheat fibres. They had a reticulate surface and contained some small spiral vessels. They were believed to be seeds, but their origin and identity could not be ascertained.

Mr. D. M. FREELAND said that the authors' figures indicate that wheat left standing some time before being milled showed increased counts of "impurities" in the flour. This seemed to call for improvement in the farmer's technique. With biscuit flours the tests also showed appreciable quantities of sandy and earthy matter in flour; if millers could once more resort to wheat washing before milling, much of this, together with excreta and insect fragments, would be eliminated. Had the authors found that the pancreatin used varied much in quality and, if so, did they recommend the use of any particular brand?

Mr. P. S. ELIAS, in replying to questions, said that the authors had no experience of seasonal variation in the hair content of rodent faeces. From the large number of such pellets examined the figure seemed to be reasonably constant. Whether the hairs came from faeces in the grain or from direct contact with rats and mice was of little consequence, as there was bound to be contamination if rodents had access to flour.

Mr. BRADSHAW said that, taking into account the length of time necessary to make each count, it was not practical, or indeed desirable, to spend additional time identifying the insect from which each fragment was derived. There was no evidence as far as he knew to show that rodent contamination of

cereals suffered from any seasonal fluctuations. The distribution of rodent hairs throughout a bulk of flour was already under consideration and 25 samples, each from the same bag of flour, were being examined. As to variations in the quality of pancreatin, there was no evidence to suggest that this had caused difficulties in the test. Oriental grain had not so far been examined.

Mr. THACKRAY said that the authors had no experience of the chloral hydrate method suggested by Mr. Heron, but he wondered whether this treatment would cause swelling of the hairs and undesirable distortion. He agreed that it was desirable to concentrate the dirt as far as possible, but an area about 4 inches in diameter was as small as it was desirable to go to in view of the amount of bran, especially in present-day flours. As to the presence of eggs, a few had been observed. Quite a large number of larvae had been noticed, including larvae from the house fly. About Mr. Manley's observations on milk he thought that the absence of rodent hairs was conclusive evidence that material found in the milk did not contain rodent faeces.

Dr. AMOS, replying to Dr. Coppock's query, said that the data given in the paper showed that the presence of 4 to 5 rodent hairs per 100 g. of flour would correspond to the presence of one fragment of mouse excreta of about 20 mg. weight in about 6 lb. of wheat. Although this might seem to some people a high contamination, he had recently seen in the West Country native English wheat which, in the small sample examined, contained one fragment of rodent excreta in each 300 to 400 g. of wheat. He knew of no experimental evidence on the effects of passage through an Entoleter upon rodent hairs present in the stock, but he did not think it likely to break the hairs into small fragments. Insects, however, were likely to be disrupted on passing through an Entoleter, with a consequent increase in the insect fragment count of the stock, but trials were being made in America on wheat with strongly aspirated Entoleters, with a view to removing the insect fragments produced by the machine. Results had been encouraging and developments along these lines might be expected. Dr. Amos said that the point raised by Mr. King was an interesting one, but no information was available upon the relation between the rodent hair contamination and the bacterial population of flour. If a flour were grossly contaminated with rodent excreta, it might exhibit a significantly high bacterial count, but he did not think it likely that there would be a positive correlation between the two factors in normal commercial flours. Bacteriological studies which he had made some years ago revealed that by far the majority of the bacteria present in flour were epiphytic micro-organisms from the wheat, and the numbers of such organisms on different types of wheat—and wheats substantially free from rodent excreta—varied so widely that the bacterial population of the resulting flour could not serve as a reliable index of rodent contamination. Dr. Amos said that he thought that Mr. Claremont was correct in his assumption that generally speaking the smaller and older mills would have a more difficult task than the large modern mills in maintaining the contamination of their flour at a low level. Many of the older and smaller mills were constructed partly of wood and would be much more difficult to render rodent-proof than the brick and concrete mills built to modern design. Moreover, in normal circumstances, many country mills would employ a considerably higher proportion of native wheat than would the large port mills, and native wheat was the worst offender as a source of rodent excreta. In reply to Mr. Raynes, Dr. Amos said that the Food and Drug Administration in America had not divulged what standards they had adopted for rodent hair and insect fragment contamination. An American chemist had, however, stated in a private communication, that there was no tolerance, but there was reason to believe that, at the moment, exception would only be taken to the presence of more than 5 rodent hairs per lb. of flour. The data presented in the paper, which included some American flours, indicated that such a standard was at the present time not always being attained.

The Separation of Hyoscine and Hyoscyamine and the Alkaloidal Assay of *Duboisia SPP.*

BY E. M. TRAUTNER* AND M. ROBERTS

THE two alkaloids hyoscyamine (with which is included atropine) and hyoscine occur together in several of the *Solanaceae*, and are usually determined as total alkaloids and calculated in terms of one or the other. A survey of the literature indicates that little attention has been directed towards a procedure for the separation of such mixtures. Kuhn and Schäfer,[1] taking advantage of the fact that hyoscine is a weaker base and more soluble in ether than hyoscyamine, claim that if an acid solution of the mixed alkaloids be made slightly alkaline with sodium bicarbonate and extracted three times with ether, then the combined ether extracts contain the whole of the hyoscine together with a small proportion of the hyoscyamine. The latter can be removed by evaporating the ether solution to dryness and repeating the procedure twice, after which the final ether extract will contain all the hyoscine in a pure state. Rowson[2] found this procedure to be unsatisfactory and proposed a process of fractional

* Department of Physiology, University of Melbourne, Australia.

liberation of the hyoscine, the extraction being repeated until a sharp transition was reached between an oily alkaloidal residue (hyoscine) and a crystalline alkaloidal residue (hyoscyamine-atropine). Besides being of doubtful accuracy, this method is not applicable to quantities of hyoscine less than 20 mg.

Two methods are described in the present paper: first, an approximately quantitative separation of the alkaloids by means of chromatographic adsorption on activated silica and subsequent fractional elution and, second, the separation and identification of the components of a mixture of alkaloids by fractional precipitation of their picrates.

Experimental

(i) *Fractionation of hyoscine and hyoscyamine on a silica column*—It has been found that 6 to 10 mg. of the mixed alkaloids can be satisfactorily separated on a silica column; both hyoscine and hyoscyamine are strongly adsorbed from benzene solution but, whereas hyoscine is rapidly eluted by absolute alcohol, this solvent moves hyoscyamine only slowly.

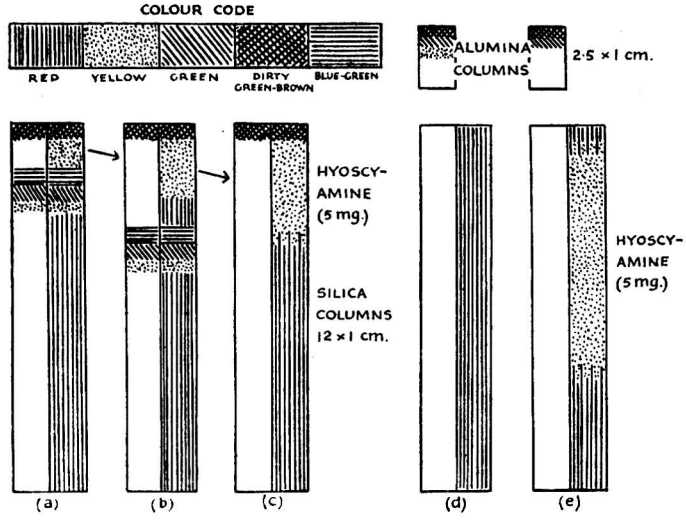

Fig. 1. Hyoscyamine-bearing *Duboisia Leichhardtii* extracts on alumina and silica. The extracts were prepared by treating the powdered material with dilute sodium carbonate and percolating with benzene. The silica columns are divided, the left-hand side showing actual positions and colours of adsorbed leaf pigments, the right-hand side the additional red and yellow zones made visible by dimethyl yellow.

Column (*a*): zones after adsorption of extract from benzene.

Column (*b*): zones after development with 10 ml. of benzene - ether mixture (1 + 1), showing adsorption-free space between alkaloids and shifted pigments.

Column (*c*): zones after washing with a little alcohol, which quickly elutes the bulk of the pigments but leaves a dirty green-brown band on top of the silica.

Columns (*d*) and (*e*) demonstrate the removal of this dirty green-brown band by a short alumina layer (indicator added to the silica only).

Column (*d*): zones after adsorption of benzene extract.

Column (*e*): zones after washing with 15 to 20 ml. of absolute alcohol. Most of the pigments are eluted through both columns by alcohol, but the silica retains up to about 4 to 5 mg. of hyoscyamine in an extended zone.

Roberts and James[3] experienced some difficulty with this procedure, for neither alkaloid can be detected on the column by viewing in visible or ultra-violet light. This was overcome and the whole investigation greatly facilitated by the observation that if a trace of dimethyl-amino-azo-benzene (butter yellow, dimethyl yellow, C.I. 19) is dissolved in the benzene solution of the alkaloids, the dye is weakly adsorbed by the silica to give a brilliant red colour, except where the alkaloids are preferentially adsorbed and there a yellow band of the unabsorbed dye is visible. By elution with ether or absolute alcohol, the dye is rapidly removed; if these solvents are then replaced by benzene or, better, light petroleum, containing a little dye, the adsorption zones reappear and it can be seen which have been eluted, separated or spread. In this way the different stages of the separation of the alkaloids from a benzene extract of a hyoscyamine-bearing *Duboisia Leichhardtii* on a silica column can be demonstrated

(Fig. 1). The dirty green-brown band at the top of the silica column is not removed by absolute alcohol; this band is retained on the alumina if the composite alumina - silica column of Roberts and James[3] is used (Fig. 1 (*d*) and (*e*)).

The most satisfactory form of silica has been found to be "Granulated Neosyl" (Peter Spence & Sons, Ltd., Widnes) in 80/100 mesh. Before use this should be carefully washed with a 50 per cent. aqueous solution of acetic acid followed by water, and, after drying, activated by calcining for 12 hours. Water and moist solvents inactivate the silica rapidly and irreversibly; hence all such materials should be thoroughly dried before use. Commercial "crystallisable" benzene is not satisfactory for use, for it occasionally gives a considerable yellow adsorption band at the top of the silica column, owing to the presence of pyrroles and other impurities; these contaminate the alkaloidal fractions and prevent clean crystallisation of the picrates. It is advisable to test all solvents used by passing a small portion through a silica column; if any visible adsorption takes place the contaminated material should be purified by passage through the column.

The efficiency of the separation of hyoscine and hyoscyamine by fractional elution from a silica column with absolute alcohol is dependent to some extent upon the dimensions of the column. That generally used in these experiments (12 cm. × 1 cm.) will allow the removal of as much as 10 to 12 mg. of hyoscine in the first 20 ml. of alcohol, while retaining up to about 4 mg. of hyoscyamine even if the volume of eluant is increased to 30 ml. If conditions are suitable, the first 15 ml. of alcohol contains the bulk of the hyoscine; the fractions between 15 and 25 or 30 ml. are almost free from bases (usually less than 0·1 mg. per 5 ml.), while hyoscyamine begins to be eluted as the volume of solvent exceeds 30 ml. (at the rate of about 0·5 to 1 mg. per 5 ml.). Removal of the hyoscyamine is more efficiently carried out by de-activating the silica with 3 to 4 ml. of 20 per cent. ammonia solution and eluting with 30 to 40 ml. of chloroform.[3]

With careful manipulation the total recovery of alkaloids by the elutions with absolute alcohol and ammoniacal chloroform combined is within 3 per cent. of the correct amount, although, if the elution be carried out in small fractions and these are determined separately, the errors of micro-titration or of colorimetry may add up to a discrepancy of 5 to 10 per cent. Again, whilst hyoscyamine is quantitatively recovered from a silica column by elution with ammoniacal chloroform, there is a small fraction of hyoscine that is not eluted by absolute alcohol, although it is readily removed by ammoniacal chloroform. The amount of hyoscine so held appears to depend upon the quantity and quality of the silica used; it is considerably reduced in the presence of hyoscyamine. Thus, with the column described above (12 cm. × 1 cm.), this amount varies from about 0·9 mg. for pure hyoscine to 0·15 to 0·3 mg. in the presence of 3 or 4 mg. of hyoscyamine. For the most efficient separation, it is advisable, therefore, to arrange that the total alkaloids submitted to the separation procedure should contain between 3 and 4 mg. of hyoscyamine; even so, the figure obtained for the hyoscyamine content will tend to be slightly high. The best results are obtained by using mixtures of alkaloids in which the ratio of the amount of hyoscine to that of hyoscyamine lies between the limits 1 : 4 and 6 : 1. The fractions obtained are pure enough to give crystalline picrates by the method described below, even when only 1 or 2 mg. of alkaloid are present.

From the above considerations it follows that a mixture of hyoscine and hyoscyamine containing less than 10 per cent. of the former cannot be separated on a silica column unless it be first submitted to a partial fractionation by some method, such as that of Kuhn and Schäfer.[1] An extract of belladonna, for example, gives the total alkaloids in the hyoscyamine fraction,[3] there usually being not more than a few per cent. of hyoscine in the total alkaloids extracted from this drug.

Results obtained by submitting mixtures of hyoscine and hyoscyamine in varying proportions to the chromatographic separation are shown diagrammatically in Fig. 2. The alkaloid in the separate fractions was determined by adding a measured excess of 0·02 *N* sulphuric acid, warming to remove excess of alcohol and any remaining benzene, and titrating the excess of acid with 0·01 *N* sodium hydroxide, using B.D.H. "4460" indicator. When extracts of solanaceous drugs are submitted to the fractionation procedure it is advisable to examine the hyoscyamine fractions titrimetrically and, in addition, by the method of Allport and Wilson,[4] employing a modified Vitali reaction, since all the stronger bases collect in the hyoscyamine fraction. This is particularly true of *Duboisia spp.*, since here the proportion of alkaloids other than hyoscine and hyoscyamine is often considerable and cannot be neglected.

(ii) *Fractional precipitation of crystalline picrates from a mixture of hyoscine and hyoscyamine*—It has been observed by Trautner, Neufeld and Rodwell[5] that if a chloroform solution containing hyoscine and hyoscyamine (not less than 5 mg. of each per ml.) be titrated with a 0·05 *N* solution of picric acid in chloroform, using dimethyl yellow as indicator and slightly over-titrating to the formation of a distinct orange colour, well-formed needles of hyoscine picrate separate immediately, while hyoscyamine picrate remains in solution and can only be induced to crystallise by addition of considerable amounts of ether or light petroleum. Using trichloroethylene as solvent, these workers describe a rapid method for the assay of hyoscine - hyoscyamine mixtures based on this principle; they found that, if the concentration of the bases was about 0·1 *N*, reasonably accurate results could be obtained by weighing the precipitated picrates.

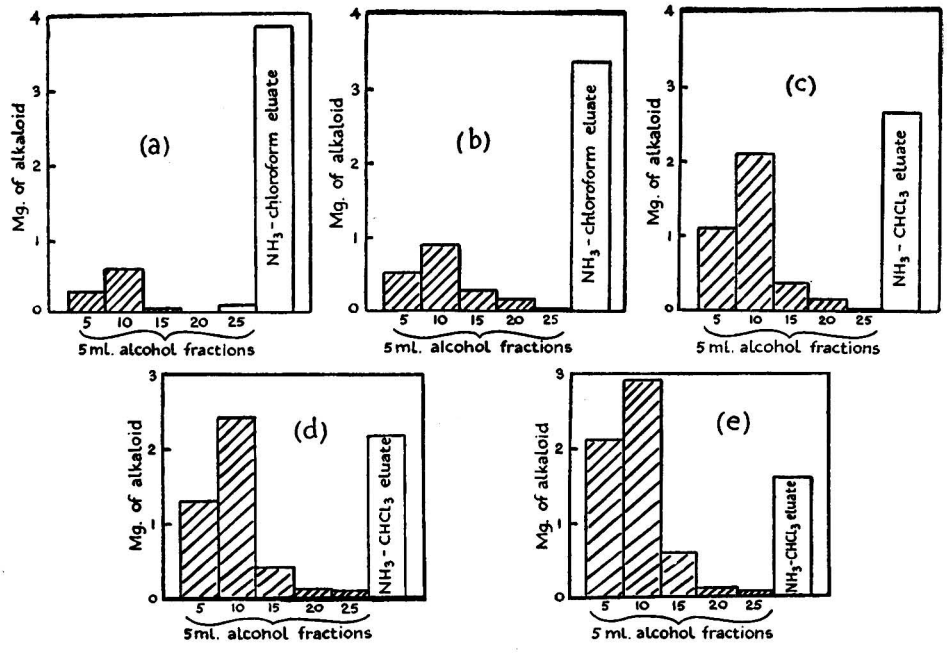

Fig. 2. Separation of hyoscine and hyoscyamine in varying proportions on silica columns (12 cm × 1 cm.). The alkaloids were adsorbed from benzene, hyoscine was washed out with 25 ml. of absolute alcohol and collected in 5-ml. fractions for titration. Hyoscyamine and any retained hyoscine were eluted with ammoniacal chloroform and estimated after removal of solvent. Titration values are represented by blocks, shaded for hyoscine and unshaded for the fraction eluted by ammoniacal chloroform. The mixtures used in the experiments had the following composition given in mg. hyoscine + mg. hyoscyamine:

(*a*) 1·03 + 4·02 (total alkaloids recovered, 4·90 mg.).
(*b*) 2·06 + 3·22 (recovered, 5·15 mg.).
(*c*) 4·11 + 2·41 (recovered, 6·36 mg.).
(*d*) 5·14 + 1·61 (recovered, 6·47 mg.).
(*e*) 7·20 + 0·80 (recovered, 7·46 mg.).

If this procedure is applied to a solution of hyoscine in chloroform containing 0·5 mg. per ml., no precipitation of the picrate takes place; however, addition of an equal volume of benzene (AnalaR grade) causes small clusters of crystals to be deposited within 24 or 48 hours and the separation is usually quantitative. A similar treatment applied to a solution of hyoscyamine in chloroform containing the highest concentration possible in a small-scale assay, about 5 mg. per ml., does not cause any precipitation, even when the proportion of benzene is increased three or fourfold. To precipitate hyoscyamine picrate it is necessary to add sufficient ether or light petroleum to produce a persistent milkiness and then, on standing, an initial crop of stout prismatic crystals forms in clusters; if the base is in the racemic form (atropine) the picrate crystallises similarly in thin blades. The separation of hyoscyamine picrate under these conditions is not quantitative; further crops of crystals are obtained on continued addition of ether or light petroleum, and a total of three to four

volumes of light petroleum are necessary to give almost complete precipitation, but it is not advisable to add this amount of solvent at one time because this tends to cause the hyoscine picrate to separate as an oil, which crystallises slowly and badly.

A solution containing only 0·3 mg. of hyoscine per ml. will give a satisfactory separation of the picrate but, if hyoscyamine or other solanaceous alkaloids are present, this minimum concentration may rise to as much as 2 mg. per ml. according to the relative proportions of the bases (see Table I). The alkaloid fractions obtained by the separation of a mixture with a silica column are sufficiently pure to form picrates that are readily identifiable by melting point, if not less than about 0·5 to 1·0 mg. of total bases is present. After washing with fresh portions of the same solvent mixture as that from which precipitation occurred, followed by drying at 105° C., hyoscine picrate usually melts at the correct temperature, 187° to 188° C.; the hyoscyamine picrate is frequently less pure and may melt at a temperature several degrees lower than the correct value, 165° to 166° C.

TABLE I

Proportions of hyoscine to hyoscyamine	Minimum concentration of hyoscine separable as picrate mg. per ml.
10 : 0 (pure hyoscine)	0·30
7 : 3	0·35
5 : 5	0·50
3 : 7	1·0
1 : 9	1·0–2·0

In their unpublished work on *Duboisia spp.*, Trautner and Rodwell developed an alternative procedure in which the picrates are crystallised from a two-phase system. The mixture of alkaloids in ether solution is poured carefully over an equal or smaller volume of water containing excess of picric acid. A cloud forms at the junction of the layers and, on standing overnight, well-shaped crystal clusters separate at the interface and on the walls of the containing vessel in both phases. This method is useful in certain circumstances because it effects a partial separation from minor alkaloids and allows crystallisation of the important bases when, with a single-phase system, only oily products are formed. By this two-phase procedure, *nor*-hyoscyamine has occasionally been found in hyoscyamine fractions, but with less than 30 to 50 mg. of alkaloids reliable results cannot be obtained.

The separation of hyoscine and hyoscyamine picrates as described above is too slow to be of practical analytical importance, since a better and more rapid fractionation can be achieved with a silica column. It is, however, useful if it is necessary to establish the identity of the main alkaloid present in the hyoscyamine fraction.

APPLICATIONS

(i) *Assay of a sample of Duboisia myoporoides (Queensland, Australia)*—About 0·5 g., accurately weighed, of powdered leaf was moistened with dilute sulphuric acid and washed with ether to remove the greater part of the ether-soluble matter and the alkaloids were extracted by treating the washed drug with a mixture of equal volumes of chloroform, previously saturated with ammonia gas and ether. The extract was evaporated to dryness, the residue dissolved in chloroform, the solvent removed and the residue again dissolved in chloroform. The proportion of non-volatile bases present was approximately determined by titration with *p*-toluene sulphonic acid in chloroform, using dimethyl yellow as indicator. The end-point was not sharp, but the volume of acid used corresponded to between 17 and 20 mg. of total alkaloids calculated as hyoscine. After a further purification of the total alkaloids by transferring to dilute acid and then to ether, the mixed ether extracts were dried, the solvent was removed and the residue dissolved in 25 ml. of benzene.

The alkaloids were separated by transferring 10 ml. of this benzene solution to a chromatograph column[3] consisting of a 2·5-cm. layer of activated alumina (type H, from Peter Spence & Sons, Ltd., Widnes; activated by treating with 50 per cent. acetic acid, washing with distilled water and, after drying, calcining for 24 hours) arranged above a column of activated silica, the dimensions of which approximate to 12 cm. × 1 cm. The alumina does not retain the alkaloids from alcohol, but adsorbs colouring matter and much other material. The

combined column was eluted with one 15-ml. portion and two 5-ml. portions of absolute alcohol. The second and third fractions were almost free from bases (less than the equivalent of one drop of 0·05 *N* acid) and were discarded. The layer of alumina was then removed and the silica eluted with 40 ml. of ammoniacal chloroform.

The alcohol fraction was diluted to 25 ml. and the tropic esters determined on a 1-ml. aliquot part by the colorimetric method of Allport and Wilson[4]; this gave a value of 1·26 mg. per 10 ml. of original benzene extract of the drug, calculated as hyoscine. The remainder of the fraction was quickly evaporated to dryness under reduced pressure, dissolved in 2 ml. of chloroform and slightly over-titrated with 0·05 *N* picric acid in chloroform. An equal volume of benzene was then added. No cloudiness appeared and, after a few hours, several drops of light petroleum were added. On allowing to stand overnight clusters of small needles separated which, after washing with a mixture of equal volumes of chloroform and benzene containing several drops of light petroleum and drying at 105° C., melted at 186° to 188° C.; after admixture with stock hyoscine picrate, the melting point was 185° to 188° C.

The ammoniacal chloroform eluate was made up to exactly 50 ml. with chloroform and 1 ml. assayed by the modified Vitali reaction[4]; this indicated a total alkaloid content of 4·1 mg. per 10 ml. of the original benzene extract, calculated as hyoscyamine. The remaining 49 ml. of the eluate was divided into two portions of 25 and 24 ml.; the 25-ml. portion was evaporated to dryness, the residue dissolved in a little alcohol and the bases titrated, giving a figure equivalent to 4·5 mg. per 10 ml. of the original benzene solution, calculated as hyoscyamine; the 24-ml. portion was evaporated to dryness, re-dissolved in chloroform, just over-titrated with picric acid as above and, after addition of one volume of ether and one volume of light petroleum, the milky mixture was left overnight. A few oily drops collected at the bottom of the container and several clusters of stout prisms were deposited on the walls. The latter, after washing and drying as described above, melted at 163° to 164° C., and the mixed melting point with stock hyoscyamine picrate was 164° to 165° C.

The figures obtained above indicate the presence, in 1 g. of original drug, of 6·3 mg. of hyoscine by the colorimetric procedure, 20·6 mg. of hyoscyamine by the same method and, from the difference between the colorimetric and titritmetric assays applied to the ammoniacal chloroform eluate, about 2 mg. of bases not esterified with tropic acid. Two small fractions containing, possibly, between 1 and 2 mg. of alkaloid (calculated for 1 g. of drug) were discarded. Since a small loss of hyoscine is usually incurred, it can be concluded that the sample of *Duboisia myoporoides* contained about 2 per cent. of hyoscyamine, 0·7 per cent. of hyoscine and 0·2 per cent. of other alkaloids.

(ii) *Starvation experiment on leaves of Atropa belladonna*—(This experiment is taken from a series of investigations carried out by Dr. W. O. James, Oxford Medicinal Plants Scheme, Department of Botany, University of Oxford. The present report deals only with the isolation and identification of the alkaloids.)

Detached leaves of *Atropa belladonna* were kept in the dark in water until they showed distinct yellowing; the material was then dried and powdered. Two portions, each 0·5 g., of the powdered drug, were assayed by the method of Roberts and James,[3] the total alkaloid content being determined by titration and the tropic ester content by the colorimetric procedure. The results of the two assays were identical and little different from the values for the untreated leaves.

The portion used for the titration was made alkaline, the alkaloids were extracted with several portions of chloroform and the combined extracts evaporated to a small bulk and slightly over-titrated with picric acid as described above. On standing, no precipitation took place, even after mixing with one volume of benzene and one-quarter volume of light petroleum. On addition of sufficient light petroleum to produce a distinct cloudiness, oily drops separated on the glass walls and, on replacing the supernatant liquid by a mixture of chloroform, ether and light petroleum having the same composition and leaving overnight, these oily drops crystallised in clusters of stout prisms. The fluid was decanted and a further quantity of light petroleum was added to it; this produced an additional crop of small prisms. A further crop could not be obtained. After washing and drying as already described, the crystals from both crops had an identical melting point, 164° to 165° C., which was slightly raised by admixture with stock hyoscyamine picrate.

The above results suggest that, under the conditions of the experiment, *i.e.*, starvation to the point of incipient proteolysis, the hyoscyamine content of leaves of *Atropa belladonna* is unchanged and neither hydrolysis nor demethylation takes place to any appreciable extent.

SUMMARY

The adsorption zones of the solanaceous alkaloids and other colourless bases can be demonstrated on columns of activated silica by displacement against dimethylamino-azobenzene (dimethyl yellow). This dye is weakly adsorbed from benzene or light petroleum to give a brilliant red colour on the column; if, however, the dye solution also contains colourless bases, or if the latter have previously been adsorbed from more polar solvents, yellow bands of unadsorbed or displaced dye indicate the position of the adsorbed bases on the column.

Both hyoscine and hyoscyamine are strongly adsorbed from benzene solution by silica, but, whereas the former is rapidly eluted by absolute alcohol, the latter is moved only slowly. It is shown that, making use of this principle, hyoscine and hyoscyamine can be separated almost quantitatively so long as the hyoscine/hyoscyamine ratio lies between 1 : 4 and 6 : 1.

The identity of 0·5 to 1 mg. of pure hyoscine or hyoscyamine can be established by preparing the picrates from chloroform solutions. By applying a preliminary chromatographic fractionation it is possible to separate and identify the components of a mixture of hyoscine and hyoscyamine when the amount of total alkaloid is between 5 and 10 mg.

The authors wish to thank Dr. W. O. James for the opportunity to carry out this work in the laboratories of the Department of Botany, Oxford. They would also like to express to Mr. N. L. Allport their appreciation of his interest in the investigation and to Mr. John Allen their thanks for his generous help during preparation of the manuscript for publication. Financial support was provided by the Oxford Medicinal Plants Scheme.

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OXFORD MEDICINAL PLANTS SCHEME
DEPARTMENT OF BOTANY
THE UNIVERSITY, OXFORD

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Application of the Dumas Micromethod to Pasture Nitrogen Analysis

BY E. P. WHITE,* F. B. THOMPSON† AND (MISS) N. BRICE†

EXTRAORDINARILY high Kjeldahl nitrogen values obtained on pasture samples from experimental plots at the Soil Fertility Research Station, Hamilton,[1] led to doubt as to the interpretation of the analytical results. These Kjeldahl values were further verified by officers of Ruakura Animal Research Station, Hamilton. All these workers employed the very effective selenium - potassium sulphate catalysts. It then seemed of interest to investigate the samples by the Dumas (absolute) method.

There is an extensive literature on comparison of the two methods when applied to various "natural materials." In general, the Dumas method has given higher values than the Kjeldahl, but in some instances this has been due to inability of the Kjeldahl method, without effective catalysts, to convert the nitrogen of some compounds completely into ammonia. In some instances values by the two methods are reported to agree well. It is also known that certain compounds can give high Dumas values, particularly with earlier forms of tube fillings.

Difficulties are often encountered in the standard Dumas method, owing to the formation of "nitrogenous charcoals" which cannot be burnt completely by copper oxide alone. Numerous modifications have been used to obtain better results with "natural materials," including addition of lead chromate, manganese dioxide or potassium dichromate, use of the Dennstedt method, addition of copper acetate for certain pyrimidines[2] and the use by

* Ruakura Animal Research Station, Hamilton, New Zealand.
† Soil Fertility Research Station, Hamilton, New Zealand.

Wiedemann of a "tapping" technique in which the material is burnt normally and then tapped to cause mixing with new copper oxide and re-heated. This method is stated to be of value for chlorophyll and ergot derivatives[3] and is reported to be excellent for plant substances.[4] A further method consists of burning as usual and then generating oxygen gas from potassium chlorate and re-burning: this method has been used for nitrogen in coal[5] and for pyrimidines.[6]

Methods used

The pasture samples were all air-dried and finely ground. The nitrogen results are all expressed as percentages of the dry weight, which was determined by drying fractions of the samples at 105° C. for 18 to 20 hours.

The Kjeldahl technique involved digestion of 100 to 105 mg. of air-dry pasture with 4 ml. of concentrated sulphuric acid, 1·37 g. of potassium sulphate and 0·03 g. of selenium. The solutions usually cleared in 30 minutes and digestion was continued for a further 80 minutes. The quantities of reagents used are based on a compromise between numerous techniques described in recent literature for Kjeldahl digestions, with various catalysts. It had previously been found that an "after-clearing" time of 80 minutes was the minimum period required to give maximum nitrogen values and that the use of selenium and mercury together did not give maximum results any more quickly than the digestion method outlined above.

An aliquot of the digest was distilled in a modified Parnas - Wagner apparatus in which the outer jacket served as the steam trap and to heat the solution. The ammonia was absorbed in boric acid and titrated with 0·01 *N* acid, using bromocresol green - methyl red indicator.

For the Dumas method, 8- to 10-mg. samples were used and the three modifications: "standard," "tapping" and "chlorate" were compared. The tube filling of copper oxide and copper gauze was that described by Niederl,[7] and Pregl,[4] and an electric furnace was used as "long burner," with a micro-burner for the combustion of the sample. For the "standard technique," after the initial burning (20 to 30 minutes) and the beginning of "sweeping out," a rapid second combustion (10 minutes) as described by Niederl[4] was used.

In the "tapping technique"[4] the standard combustion was first carried out and then the tube was tapped vigorously so as to mix up the reduced portions and a second, high-temperature combustion was done carefully before the sweeping out.

For the "chlorate technique,"[6] an extra short roll of copper gauze was inserted in the centre of the packing and replaced after each combustion. The standard technique was first carried out, including full sweeping out; about 50 mg. of potassium chlorate in a platinum boat at the end of the tube were then heated, with the tap of the Kipp turned off, and the reduced portions in the tube were heated strongly until re-oxidation was complete, the bubble-rate being kept within prescribed limits all the time. Sweeping out then produced a further quantity of nitrogen. The method also has the advantage of cleaning the tube, which otherwise has a limited life owing to much copper being formed with materials of this nature.

Results

Values obtained by the Kjeldahl method and the three modifications of Dumas technique are presented in Table I. Kjeldahl results are from routine laboratory determinations, without precautions for extreme accuracy. Since the nitrogen determinations in the different columns of Table I were made at different times, separate determinations of dry matter were made on each pasture sample for each technique. Thus small variations in results may be partly due to differences in the dry matter contents. Pasture samples Nos. 1 to 7 are from the experimental plots previously mentioned and Nos. 8 and 9 from Ruakura cow pasture.

The standard Dumas method gives results that are low and haphazard, the rate of burning appearing to have a considerable influence on the value obtained. With the "tapping" technique the values are still erratic, but often considerably higher, whilst the "chlorate" technique gives values that are higher and repeatable within the limits expected of the method and of a possible small sampling error. One value obtained with use of copper acetate did not differ appreciably from those obtained by standard technique. The "chlorate" method gives values in approximate agreement with those obtained by the Kjeldahl method, and leaves little doubt that the values obtained by the Kjeldahl method actually represent nitrogen.

The "chlorate" technique is to be recommended for its effectiveness in analysis of difficult materials, *cf.* Belcher,[8] but owing to the long time taken to complete a determination, 3 to 3½ hours, and a possible small sampling error in taking 10 mg. of pasture sample, it is not to be recommended for routine pasture analysis.

TABLE I

PER CENT. OF NITROGEN IN PASTURE

Sample No.	Kjeldahl method		Dumas method		
	S.F.R. Station	Ruakura Station	Standard technique	Tapping technique	Chlorate technique
1	5·48		5·28; 5·12; 4·23; 4·69	4·88	5·30; 5·20
2	5·74		4·82; 4·90; 4·63; 4·93	5·46	5·30; 5·57
3	6·21		4·68; 5·20; 5·31	5·98	5·94; 6·00
4	6·07		4·80; 5·47; 5·52	5·82	6·09; 6·04
5	6·57		5·71; 5·15; 5·98; 5·62	5·73; 5·83	6·10; 6·20
6	5·96; 5·95	6·14; 6·12	4·83; 5·36; 4·97; 4·73	5·80; 5·70; 5·58	6·21; 6·05
7	6·06; 6·04	6·06; 6·06	4·81; 5·47; 4·71	5·93	6·10
8	3·70; 3·70	3·77; 3·82	3·20; 2·95; 3·25; 3·60	3·43	3·74; 3·81
9	3·78; 3·88	3·95; 3·87	3·22; 3·30; 3·43; 3·53; 3·74	3·50; 3·74; 3·43; 3·73	4·07; 3·96
Hippuric acid analytical standard N = 7·82%	7·79; 7·76	7·91; 7·79	7·94; 7·86; 7·87; 7·79	7·83; 7·86	7·83; 7·85

SUMMARY

Nitrogen in pasture samples has been determined by the Dumas method. The standard technique is inadequate, "tapping" technique is little better, and the only reliable method tried is that in which the reduced residue is re-burnt in oxygen and the extra nitrogen collected. The latter technique gave repeatable values in close agreement with those of the Kjeldahl method using selenium - potassium sulphate catalyst. Extraordinarily high nitrogen values (6·0 to 6·5 per cent.) on pasture are reported.

We have to thank Mr. M. R. Coup and Mr. M. Gothorp of Ruakura Animal Research Station for carrying out Kjeldahl determinations recorded in the third column of the Table I, and for pasture samples 8 and 9.

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CHEMICAL LABORATORIES
RUAKURA ANIMAL RESEARCH STATION
and SOIL FERTILITY RESEARCH STATION
DEPARTMENT OF AGRICULTURE
HAMILTON, NEW ZEALAND

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A Method for the Determination of Minute Amounts of Zinc in Alloys used for making Lead Pipes and Cable Sheathing*

By B. S. EVANS

In 1935 a specification for lead pipes (B.N.F. Ternary Alloy No. 2) was published.[1] This demanded an upper limit of 0·01 per cent. for zinc. The composition of the alloy is:—

Tin, 1·25 to 1·75; Cadmium, 0·2 to 0·3; Lead, remainder.

In 1938 a similar specification[2] required an upper limit of 0·002 per cent. of zinc for the various alloys specified. These alloys were four in number and their compositions were:—

	Tin	Antimony	Cadmium	Lead
"A"	1·8 to 2·2	—	—	Remainder
"B"	—	0·8 to 0·9	—	"
"C"	0·35 to 0·45	—	0·12 to 0·18	"
"D"	—	0·45 to 0·55	0·2 to 0·3	"

As no chemical method for the determination of so small an amount of zinc in such alloys was then available, page 7 of the 1938 specification includes the sentence, "The impurities shall be determined by spectrographic methods." This is obviously an unsatisfactory position from the point of view of the analyst, as not only does it require expensive apparatus and special technique, but also the standardisation of the standards required is a serious problem in itself. The following method is put forward therefore as providing a means for chemists to determine these small amounts of zinc in the alloys without recourse to any apparatus beyond that found in an ordinary laboratory.

The difficulty of the determination required is of course due to the very minute amount of zinc to be determined, but this difficulty is much enhanced by the fact that many cable-making alloys contain cadmium as a constituent in amounts up to 100 times the significant amount of the zinc. Furthermore, the diphenylcarbazone adopted as an indicator for the final titration of the zinc produces a similar colour with minute amounts of cadmium, which upsets the titration. Separation from cadmium must therefore be, not merely good, but complete.

The solution to these difficulties here offered is as follows:—

(*a*) *Separation of the zinc*—Separation from the main bulk of lead and from tin and antimony follows the ordinary lines; separation from cadmium and from residual amounts of lead is based on the following observations:—

(i) Whereas zinc sulphide in common with lead and cadmium sulphides can be precipitated in presence of alkali cyanides and absence of ammonium salts, if a good excess of ammonium salt is present the zinc cyanide complex is not broken up and zinc remains in solution, whilst lead and cadmium are precipitated.[3]

(ii) It has been found that the zinc ammonium cyanide complex is broken up by acetone, which presumably destroys the cyanide with formation of acetocyanhydrin. Accordingly, if excess of acetone is added to the bright filtrate obtained from the treatment described in the preceding paragraph, after a while zinc sulphide comes down as a pure white precipitate.[3]

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* Communication from the Armament Research Department, late The Research Department, Woolwich.

(iii) The above separation has been found to be complete in one operation. If, however, for any reason it is considered desirable to repeat the separation, 0·002 g. of lead in solution should be added to the *aqua regia* solution of the zinc sulphide and the separation carried out as before. This lead is to act as a collectant for any trace of cadmium that may be present.

(*b*) *Determination*—The very minute amounts of zinc involved require special treatment. The titration with 0·001 *M* ferrocyanide which has been described in an earlier communication has been found excellent for this purpose; as 1 ml. of 0·001 *M* ferrocyanide ≡ 0·00013086 of Zn, 0·001 per cent. of Zn on a 10-g. sample requires 0·76 ml.[4]

As some of the reagents employed, especially the sulphide - cyanide mixture, extract zinc readily from the glass of apparatus, it is absolutely essential that all apparatus used must be made of a glass that does not include zinc in its formula. In the trial determinations made for this paper only Pyrex glass was employed.

Method

All cable-making alloys appear to contain either tin or antimony (or both), which it is necessary to remove before proceeding to the precipitation of zinc sulphide, because (i) either element hinders the precipitation of zinc sulphide from ammoniacal solutions,[5] and (ii) by similarly hindering the precipitation of cadmium sulphide it prevents the adequate separation of cadmium from zinc, which is an essential part of the method.[5]

For tin an adequate separation is provided by the mere solution of the alloy in nitric acid, and the precipitated "metastannic acid" does not co-precipitate zinc. Antimony, in absence of tin, is either not separated or only very partially separated by this method; consequently the method must be treated under two headings:—

(*a*) When antimony is absent.

(*b*) When antimony is present. This is the same method with intercalation of a hydrogen sulphide separation of the antimony.

Method A. In absence of antimony—Dissolve 10 g. of the alloy in 100 ml. of nitric acid (sp.gr. 1·2) diluted with 100 ml. of water; filter off the precipitated "metastannic acid" and wash with 5 per cent. nitric acid. Add 20 ml. of diluted sulphuric acid (1 + 3), stir thoroughly and cool completely; filter off the lead sulphate precipitate and wash with 2 per cent. (v/v) sulphuric acid. Add a piece of litmus paper to the filtrate and then aqueous ammonia (sp.gr. 0·88) until the paper remains dark blue after shaking; add 20 ml. of 10 per cent. potassium cyanide solution, and then, after shaking, a mixture of 10 ml. of 10 per cent. potassium cyanide solution and 10 ml. of 10 per cent. sodium sulphide solution, shake and heat *just* to vigorous boiling.[3] As boiling with ammonium salts rapidly destroys cyanide with production of a brown product, prolonged boiling will cause zinc sulphide to precipitate from this mixture, consequently care must be taken that the solution is only just allowed to reach vigorous boiling and is then immediately removed and cooled. After cooling, filter off the precipitated lead and cadmium sulphides; make a mixture of 20 ml. of 20 per cent ammonium nitrate solution, 10 ml. of 10 per cent. potassium cyanide solution and 10 ml. of 10 per cent. sodium sulphide solution and pour, in two portions, through the precipitate on the filter; finally wash the precipitate four times with 5 per cent. ammonium nitrate solution and discard it. Add to the filtrate 60 ml. of acetone, shake well and allow to stand for 15 minutes; any white turbidity at the end of this time is due to zinc sulphide, but even if the turbidity is not visible the process should be continued because in this rather large dilution the zinc sulphide is not always easy to see. Add a little paper pulp to the liquid, shake well and allow to stand for a further five minutes, then transfer to the steam-bath and allow to stand over the open steam for 15 minutes longer; finally again shake and cool completely.[3] Filter off the pulp with any precipitated zinc sulphide on a tightly packed pulp filter; the liquid filters excellently in spite of its unpromising appearance and the filtrate should be brilliant. Wash with 5 per cent. ammonium nitrate solution, discard the filtrate and transfer the funnel containing the filter to a titration flask. The best form of titration flask is a 250-ml. Erlenmeyer Pyrex flask with a ground-in stopper, but if this is unobtainable

an ordinary white glass-stoppered bottle will serve. The advantage of the flask shape is that inversion makes it far easier to compare the colour of the solvent that runs down into the neck than if a bottle is used. Two similar flasks or bottles are required for each titration, one to hold the sample and the other the blank. Place 20 ml. of diluted *aqua regia* (25 ml. of nitric acid + 75 ml. of hydrochloric acid + 100 ml. of water) in the empty precipitation flask which held the zinc sulphide before filtration, and a second 20 ml. in the blank titration flask, heat the first portion to boiling and pour, in two portions, through the filter, receiving the liquid in the other titration flask; care must be taken that all the precipitate on the filter is attacked. Rinse-in the precipitation flask with hot water and wash the filter four times; retain the two titration flasks and discard the filter. Add water to the blank titration flask until the volumes are approximately equal.

Method B. In presence of antimony—Dissolve 10 g. as for method A, and filter if necessary; neutralise the filtrate with ammonia, make just acid with concentrated nitric acid and add 5 ml. in excess; add 100 ml. of 20 per cent. sodium sulphate ($Na_2SO_4.10H_2O$) solution, cool, filter and wash, as for method A. Place the filtrate in a beaker marked at 150 ml., add 10 ml. of concentrated nitric acid and boil down to the 150 ml. mark; cool, pass hydrogen sulphide for 15 minutes; filter off the antimony sulphide without undue delay, wash with 5 per cent. ammonium nitrate solution and discard the precipitate. Boil the filtrate until the hydrogen sulphide is expelled, cool, and from here on treat exactly as the filtrate from the lead sulphate in method A.

Titration—By either method we have now got the whole of the zinc from the 10-g. sample dissolved in one of the titration flasks with 20 ml. of diluted *aqua regia* and four washings with water; in the other titration flask are 20 ml. of the same batch of *aqua regia* and an amount of water to make the volumes approximately the same. Put a small piece of litmus paper into each flask and add diluted ammonia (1 + 1) until on shaking the papers turn blue; add from a dropping bottle diluted nitric acid (sp.gr. 1·2) till the papers just turn red; then cool. When cold add diluted ammonia (1 + 1) from a dropping bottle drop by drop with intermediate shaking, until one drop turns the paper from red to the first shade of mauve. Add to each flask 15 ml. of 0·2 *N* sodium carbonate solution followed by 4 drops of 10 per cent. potassium cyanide solution; then add 10 ml. of acetone, stopper, shake and allow to stand on the bench for 15 minutes. Into each flask place 10 ml. of a mixture of amyl alcohol and carbon tetrachloride (50 + 50) and run in 0·1 ml. of a 1·5 per cent. solution of diphenylcarbazone in alcohol, shake each flask vigorously for 15 seconds and allow to settle out. The solvent in the blank flask should now be coloured a pale brownish-orange, while that in the sample flask, if zinc is present, will be coloured more or less red, dependent on the amount of the zinc. Titrate the sample flask with 0·001 *M* potassium ferrocyanide solution, shaking vigorously for 15 seconds after each addition and allowing to settle out before comparing with the blank, which meanwhile is left standing on the bench. Comparison is best made by inverting the two flasks and looking through the necks. The end-point is when all the red colour has been titrated out of the sample flask, but the colour in the solvent in this flask should be if anything slightly paler and yellower than the blank at the end-point. If, as sometimes happens, the solvent in the blank flask remains hazy after its one shaking it must be shaken again until it drops bright.[4]

As the amounts of zinc involved are very small and zinc is a widely spread element, it is necessary to carry out blank tests on all chemicals used; for the same reason great cleanliness is necessary and all glassware must be rinsed with acid before washing and finally rinsed with distilled water. The latter precaution is essential because magnesium gives a slight colour with carbazone under the conditions of the titration and this colour is not discharged on titration. All chemicals, and more especially the distilled water used, must be of a high degree of purity.

Trials were made on two alloys, to 10-g. portions of which various amounts of zinc had been added. The compositions of the two alloys were:—

(*a*)		(*b*)	
Lead	98·25	Lead	99·25
Tin	1·50	Antimony	0·50
Cadmium	0·25	Cadmium	0·25
	100·00		100·00

Results obtained are shown in Table I.

TABLE I

Method	Wt. of alloy taken g.	Zinc added g.	Titration 0·001 *M* $K_4Fe(CN)_6$ ml.	Zinc found corr. for blank g.	Zinc, per cent. Added	Zinc, per cent. Found
A	10·0	—	0·2	—	—	—
A	10·0	0·00010	1·0 − 0·2 = 0·8	0·00010	0·001	0·0010
A	10·0	0·00020	1·8 − 0·2 = 1·6	0·00021	0·002	0·0021
A	10·0	0·00030	2·4 − 0·2 = 2·2	0·00029	0·003	0·0029
A	10·0	0·00040	3·3 − 0·2 = 3·1	0·00041	0·004	0·0041
A	10·0	0·00050	4·0 − 0·2 = 3·8	0·00050	0·005	0·0050
A	10·0	0·00100	8·0 − 0·2 = 7·8	0·00102	0·010	0·0102
B	10·0	—	1·6	—	—	—
B	10·0	0·00010	2·4 − 1·6 = 0·8	0·00010	0·001	0·0010
B	10·0	0·00020	3·0 − 1·6 = 1·4	0·00018	0·002	0·0018
B	10·0	0·00030	4·0 − 1·6 = 2·4	0·00031	0·003	0·0031
B	10·0	0·00040	4·6 − 1·6 = 3·0	0·00039	0·004	0·0039
B	10·0	0·00050	5·4 − 1·6 = 3·8	0·00050	0·005	0·0050
B	10·0	0·00100	9·0 − 1·6 = 7·4	0·00097	0·010	0·0097

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

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August, 1947

A Study of the Cobalt-Ferricyanide Reaction with Relation to the Determination of Cobalt in Steel

BY B. BAGSHAWE AND J. D. HOBSON

THE use of potassium ferricyanide for the potentiometric titration of cobaltous salts has been investigated by Tomiček and Freiberger[1] and by Dickens and Maassen.[2] The latter authors developed the application of the method to steel analysis, for which it has also been found satisfactory by J. L. West.[3] Its extension to the analysis of cobalt smelter samples, omitting the use of perchloric acid in the absence of chromium and vanadium, has been reported by Hall and Young.[4]

In the search for a method capable of greater accuracy and reproducibility than the usual α-nitroso-β-naphthol procedure on high cobalt steels, attention was drawn to the foregoing references. In the course of our examination, certain inherent features of the ferricyanide titration were revealed which raise the question of the stoicheiometry of the reaction and which have apparently not been sufficiently recognised by other workers.

The applicability of the method and its performance for purposes of general routine are not in question; in these respects our work has served to confirm that of others, but it is important to recognise the presence of errors of a fundamental nature that are sufficient to impair the value of the process as a reference method where maximum accuracy is desired.

EXPERIMENTAL

APPARATUS—For the potentiometric titrations carried out in the course of this work, platinum and normal potassium nitrate - calomel electrodes were used. The potentials were measured by means of a Cambridge valve-voltmeter and no back E.M.F. was applied, the circuit being as shown in Fig. 1.

STANDARD SOLUTIONS—*Potassium ferricyanide*—11·7 g. of the pure A.R. grade reagent dissolved in 1 litre of distilled water.

Cobalt nitrate, $Co(NO_3)_2 6H_2O$—The A.R. grade reagent was recrystallised from 90 per cent. alcohol and an aqueous solution was prepared containing 9·671 g. of the recrystallised salt per litre.

Ammonium citrate—666 g. of citric acid were dissolved in hot water and the solution was diluted to 1330 ml. when cold. To this solution was added a mixture of 660 ml. of aqueous ammonia of sp.gr. 0·88 and 240 ml. of water. The solution prepared in this manner had a slight alkaline reaction.

Standardisation—The relative strengths of the ferricyanide and cobalt nitrate solutions were obtained by titration against each other and their absolute strengths by reference to a primary standard cobalt solution prepared from the pure electro-deposited metal.

Titrations were carried out in a solution containing 100 ml. of the ammonium citrate solution and 60 ml. of aqueous ammonia of sp.gr. 0·88 in a total volume of 400 ml.

PROCEDURE FOR STEELS—The method used was that of Dickens and Maassen.[2]

Observations — The initial experiments soon led to the conclusion that the normal electrode potential of the cobaltous-cobaltic system is too close to that of the ferrocyanide - ferricyanide system, and there results a low value for the equilibrium constant and a consequent progressive loss of definition of end-point inflection with increasing cobalt concentration, as shown in Fig. 2. From this Figure it will be seen that only at A, where comparatively small titration volumes are employed, is the end-point marked by a sufficiently sharp change of potential for its accurate determination. It is clear also that the practice of titrating to a large "kick" of the galvonometer is unsound, because this point does not coincide with the equivalence point of the reaction but is an arbitrary point on the curve in the region of B. The observations noted above were further examined and confirmed by deductions based on experimental determinations of the normal oxidation potentials of the two systems involved in the reaction

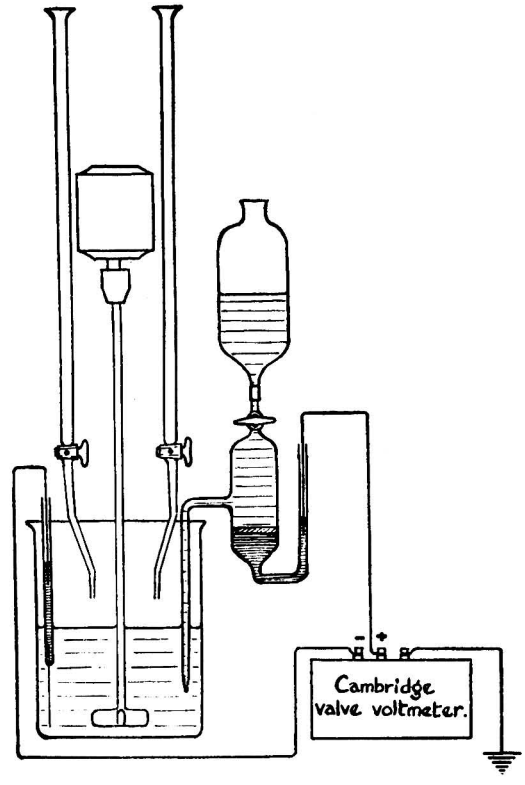

Fig. 1. Diagram of potentiometric titration apparatus.

$$Co^{\cdot\cdot} + Fe(CN)_6''' \rightleftharpoons Co^{\cdot\cdot\cdot} + Fe(CN)_6'''' \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Determination of normal oxidation potentials—To measure the normal potential of the system ferricyanide - ferrocyanide, a solution was prepared containing equimolecular proportions of the respective potassium salts, each at half the concentration employed as standard

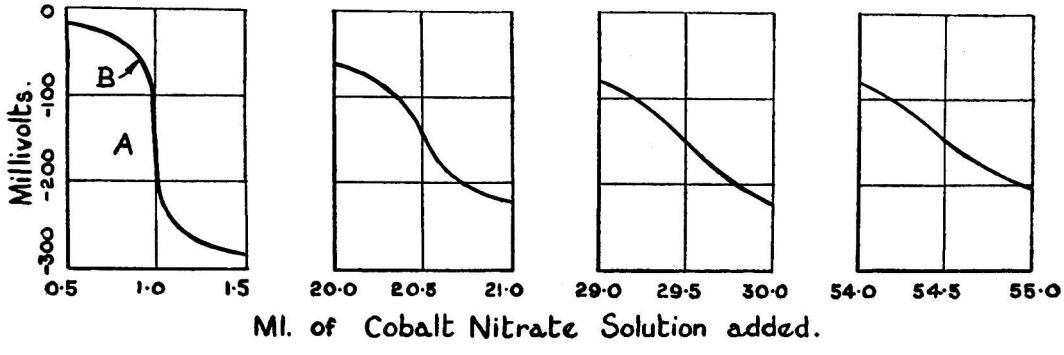

Fig. 2. Effect of cobalt concentration on End-point Inflection.

oxidant. This solution was then added to the ammoniacal citrate solution used for the titration and the potential was measured.

The cobaltous - cobaltic system was prepared by oxidising a quantity of ammoniacal cobalt nitrate solution by passing oxygen through the solution overnight, and then adding an equal volume of unoxidised cobalt nitrate solution.

The values obtained for the normal oxidation potentials of these systems in 400 ml. of solution containing 60 ml. of aqueous ammonia of sp.gr. 0·88 and 100 ml. of ammonium citrate solution and with platinum and normal potassium nitrate - calomel electrodes at 15° C. were—

Cobaltous - cobaltic system — 0·259 volt,
Ferrocyanide - ferricyanide system — 0·052 volt.

Theoretical considerations—It can be shown that if $E_1°$ and $E_2°$ are the normal oxidation potentials at 15° C., of a system taking part in a reaction, then the equilibrium constant of the reaction, K, is given by

$$\text{Log. } K = \frac{1}{0{\cdot}0571} [E_1° - E_2°] \text{ at } 15° \text{ C.}$$

From the values of $E_1°$ and $E_2°$ obtained, the equilibrium constant for the reaction of equation (1) is found to be $K = 4{\cdot}21 \times 10^3$.

Using this value for the equilibrium constant and applying the law of mass action, we have

$$\frac{[Co'''].[Fe(CN)_6''''']}{[Co''].[Fe(CN)_6''']} = 4{\cdot}21 \times 10^3$$

Suppose that in a titration of 50 ml. of cobalt nitrate solution with 50 ml. of exactly equivalent potassium ferricyanide, there are x ml. of unchanged cobaltous salt present at the equilibrium point. Then

$$\frac{(50 - x)(50 - x)}{(x) \quad (x)} = 4{\cdot}21 \times 10^3$$

whence $$\frac{50 - x}{x} = \sqrt{4{\cdot}21 \times 10^3} \text{ and } x = 0{\cdot}77 \text{ ml.}$$

Thus, 0·77 ml. of cobaltous nitrate solution remain unoxidised and 0·77 ml. of potassium ferricyanide solution remain unreduced at the point of inflection.

Similarly it can be shown that when a further 1 ml. of potassium ferricyanide solution is added, making a total of 51 ml., then 0·50 ml. of cobaltous nitrate solution still remains unchanged.

The complete oxidation potential curve of each system was investigated in a manner similar to that employed in the measurement of their normal oxidation potentials, by taking varying proportions of the two components in each system. The two systems were found to overlap, as shown in Fig. 3, thus proving conclusively that the reaction must always be a balanced one and cannot proceed to completion, since in the equilibrium set up an appreciable amount of unoxidised cobalt and unreduced ferricyanide must always co-exist.

Potentiometric titration of cobaltous salts with potassium ferricyanide has also been carried out, using a calomel electrode with normal potassium chloride solution.[2] Experiments using this electrode gave titration potential curves very similar to those previously obtained with a normal potassium nitrate - calomel electrode except that the potentials were about 0·265 volt higher throughout. The potential difference between calomel cells with normal potassium nitrate and chloride respectively was found to be 0·267 volt, thus accounting for the changed potential values. There appeared to be no reason for preference of one cell to the other.

In some further experiments on the displacement of the oxidation potentials of the two systems with variation of the titration medium, it was shown that the potential difference was increased by increasing the concentration of ammonium hydroxide, and reduced by addition of ammonium citrate. The values under the experimental conditions recommended[2] were only slightly lower than the maximum obtained during these experiments. It is therefore unlikely that any improvement in the method can be made by modification of conditions.

Effect of other elements

None of the elements commonly found in steel appear to interfere, with the exception of manganese, tervalent chromium and quadrivalent vanadium.

Manganese—In determinations of cobalt, Dickens and Maassen[2] correct for manganese on the basis of the reaction

$$Fe(CN)_6''' + Mn'' \rightarrow Fe(CN)_6'''' + Mn'''$$

In general, our work confirms the above reaction for steel solutions of known manganese content, but the stoicheiometry of the reaction appears to be affected to some extent by the

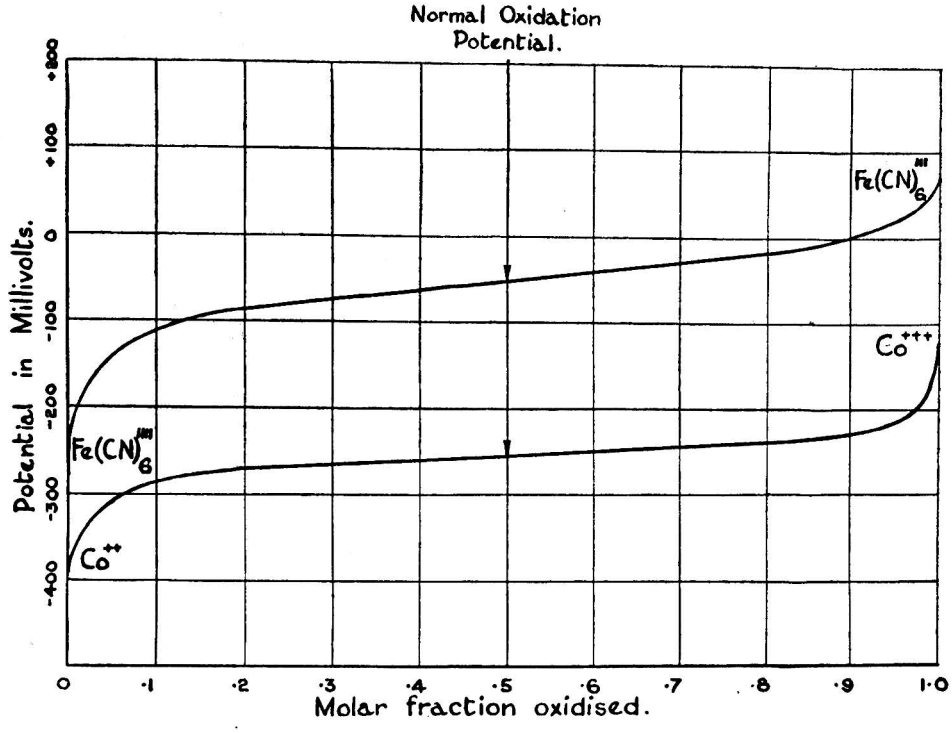

Fig. 3. Oxidation – reduction potentials of the systems cobaltous – cobaltic and ferrocyanide – ferricyanide.

concentration of other ions present in the solution. Further, we have evidence in certain instances where the reaction has proceeded stoicheiometrically according to the equation

$$O + 3MnO \rightarrow Mn_3O_4$$

This is shown in the following Table of titrations where the molar ratio of manganese to ferricyanide, 1 : 1·5, required to establish the above reaction, is almost exactly satisfied.

Table I

$MnSO_4.4H_2O$ solution ml.	$K_3Fe(CN)_6$ solution ml.	Mn mg.	$K_3Fe(CN)_6$ mg.	Molar ratio Mn : $K_3Fe(CN)_6$
36·30	25·13	70·7	282·2	1 : 1·52
41·47	27·58	80·8	309·6	1 : 1·56
39·92	27·57	77·8	309·5	1 : 1·51
35·90	25·00	69·9	280·6	1 : 1·49

$MnSO_4.4H_2O$ solution ≡ 0·001948 g. Mn per ml. (2 × factor 0·974)
$K_3Fe(CN)_6$ solution ≡ 0·01123 g. per ml. (11·7 × factor 0·960)

The foregoing values were all obtained in titrations of pure manganous sulphate solutions in ammoniacal citrate solution. In solutions of steels the molar ratio of 1 : 1 required by the Dickens and Maassen reaction is more nearly reproduced. The presence of iron tends towards the stoicheiometric value of unity for the manganese reaction, but the actual value

is influenced by the particular concentrations of manganese, iron, cobalt and perchlorate ions present in the solution.

We have not pursued further this apparently anomalous behaviour of manganese, as the Dickens and Maassen reaction appears to be sufficiently valid as a basis for correction of the manganese effect in cobalt determinations on steels; it is clear, however, that inconsistencies may arise.

Chromium—Dickens and Maassen[2] state that tervalent chromium does not interfere with the reaction between $Co^{\cdot\cdot}$ and $Fe(CN)_6'''$ in cold solution, and Tomiček and Freiberger[1] also say that there is no interference unless the solution is strongly alkaline. Both papers agree that sexavalent chromium is without influence in cold solution.

Our work conflicts with the former statement and indicates that tervalent chromium is oxidised slowly by ferricyanide in cold ammoniacal citrate solution, but agrees with the latter that there is no interference from chromate.

Since steel solutions are prepared by perchloric acid fuming preparatory to applying the titration procedure, chromium will be substantially in the sexavalent state, and hence there is little danger of titration error due to this element.

Vanadium—This is also rendered non-interfering in steel solutions by virtue of its oxidation to the quinquevalent stage by fuming perchloric acid.

Results on steels

In order to assess the practical merits of the method, a series of plain and alloy steels covering a range of low and high cobalt contents have been examined and the results compared with the results of absorptiometric determinations by the nitroso-R-salt reaction,[5] which appears to be the most accurate alternative procedure at present available for steels (Table II).

Table II

	Type	Cobalt, per cent. Potentiometric	Absorptiometric
1.	Plain carbon steel	0·03	nil
2.	Plain carbon tyre steel	0·02	nil
3.	High-speed steel, 6 per cent. W, 4 per cent. Mo, 4 per cent. Cr, 1 per cent. V	0·63	0·62
4.	High-speed steel, 16 per cent. W, 3 per cent. Cr, 1 per cent. V	4·05; 4·10	4·32
5.	C.Cr die steel, 1·5 per cent. C, 13 per cent. Cr	1·36	1·29
6.	C.Cr die steel, 1·5 per cent. C, 13 per cent. Cr	3·77	3·85
7.	High-speed steel, 20 per cent. W	16·41; 16·48	16·48
8.	High-speed steel, 20 per cent. W	16·15	16·57

The results given above for the nitroso-R-salt absorptiometric method are considered to be accurate to ±1 per cent. of the amount of cobalt present. It will be seen that the potentiometric values show variable and in certain cases marked divergence from the absorptiometric results, although for general purposes of routine checking to specification they may be considered acceptable.

Conclusion—The application of the potentiometric ferricyanide titration to the determination of cobalt in steel is for the most accurate purposes limited by inherent errors consequent on the low value of the equilibrium constant of the reacting system, and by the necessity for manganese corrections that may not always be valid. The results are sufficiently accurate for most purposes of general routine, but for accuracy and reproducibility the potentiometric method compares unfavourably with the absorptiometric nitroso-R-salt procedure, which is equally well adapted to routine requirements.

Summary

A critical survey of the method of potentiometric titration of cobaltous ion with ferricyanide in ammoniacal citrate solution has been made. The normal oxidation potentials for the $Co^{\cdot\cdot}$ - $Co^{\cdot\cdot\cdot}$ and the $Fe(CN)_6''''$ - $Fe(CN)_6'''$ systems have been determined and it is shown that the low value for the equilibrium constant of the reaction system accounts for incomplete titration at the point of inflection and for a rapid decrease of sharpness of inflection with increasing cobalt concentration.

The corresponding simultaneous oxidation of manganese according to the reaction $2MnO + O \rightarrow Mn_2O_3$ has been generally confirmed for steel solutions, but inconsistencies

have been noted and in pure manganous salt solution there has been evidence of the reaction proceeding according to $3MnO + O \rightarrow Mn_3O_4$. Tervalent chromium causes error, but there is no interference from sexavalent chromium.

Cobalt determinations have been made on a series of plain and alloy steels covering low to high cobalt contents and the results compared with values obtained by the nitroso-R-salt absorptiometric method. The comparison shows variable divergencies from the absorptiometric values, but they come within acceptable routine tolerance limits.

We are indebted to the Directors of Messrs. Thos. Firth & John Brown, Ltd., and in particular to Dr. C. Sykes, F.R.S., of the Brown - Firth Research Laboratories, for permission to publish this paper.

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THE BROWN - FIRTH RESEARCH LABORATORIES
PRINCESS STREET, SHEFFIELD, 4

September, 1947

Discussion

Mr. H. J. CLULEY said that he and his colleagues had used a modification of the method of Dickens and Maassen for the determination of cobalt in low-expansion nickel - cobalt - iron alloys used for glass-to-metal seals (Chirnside, R. C., Cluley, H. J., and Proffitt, P. M. C., ANALYST, 1947, **72**, 351). They could confirm the authors' findings that under conditions suitable for the cobalt titration there is no constant relationship between the amounts of manganese present and ferricyanide used and they had found that a preliminary separation, as dioxide, of the small amounts of manganese present in the alloys was essential. After separation of the manganese, the method for cobalt worked admirably and they had obtained rather better precision than that claimed by the authors. Since large amounts of ferric salts are detrimental, the enhanced precision obtained in the determination of cobalt in nickel - cobalt - iron alloys might be attributed to the iron-to-cobalt ratios being much lower than that normally encountered in cobalt steels.

Dr. B. S. EVANS said that there was another possible explanation of the erratic behaviour of manganese. One was inclined to focus attention on one side of the equation, but it should not be forgotten that when ferricyanide was reduced, ferrocyanide was formed. Ferricyanide was a relatively stable compound, apart from its oxidising properties, but the reactions of ferrocyanide were many and peculiar. Many of these reactions could not be expressed simply numerically and one tended to speak of "complexes" and not "compounds." In these circumstances it was quite conceivable that a substance like manganese might upset the balance of equilibrium in an unpredictable manner.

Mr. HOBSON said he was interested to hear that Mr. Cluley had encountered trouble due to the presence of manganese. He had made many experiments on the interference of manganese, but had been unable to form any satisfactory theory to explain the results. Removal of manganese was obviously the best solution, although difficult to make complete. In addition, Mr. Cluley had used smaller amounts of cobalt in his titrations, which would also aid in giving a sharper end-point.

In reply to Dr. Evans, he agreed that there might be complex formation, and there was also the possibility that cobalt or manganese might have catalytic effects on the course of the reactions.

Notes

A NOTE ON THE MEASUREMENT OF PLATING THICKNESS

THE Jet Test devised by the British Non-Ferrous Research Association[1,2] for the measurement of local thickness of coatings on plated articles has been widely adopted, for the test is rapid, simple to carry out and sufficiently accurate for its purpose. In making a determination, the flow of liquid and a stop-clock of the stop-and-go variety are started simultaneously; after 5 to 10 seconds both are stopped and the coating is examined for penetration. This process is repeated until the first signs of penetration are observed. The total time is taken as a measure of the thickness of the coating.

A rather unattractive feature of the method is the need to stop the flow before examining the coating for penetration. Furthermore, it is often difficult to detect the first signs of penetration without some experience; and the use of "spot tests" to detect the underlying metal considerably extends the time required for a thickness determination.

A. J. Lindsey and L. E. Terrett[3] have suggested the detection of the "penetration point" by recording the change of potential on exposure of the underlying metal, of the half cell formed by the plated article in contact with the jet of reagent solution. Thus, by measuring the E.M.F. of the cell formed by this half cell and a suitable reference electrode in the bulk of the reagent solution, the "penetration point" can be detected without stopping the flow of liquid and without examination of the sample. The purpose of

this note is to describe a modification of the Jet Test based on this principle, using the standard form of Jet Test apparatus and a commercial valve voltmeter.

In practice, the reference electrode which is used consists of a saturated calomel cell making electrical contact with the reagent solution through a salt bridge which temporarily replaces the thermometer in the B.N.F. apparatus. This electrode and a crocodile clip are connected to the appropriate terminals of a Mullard Electrometric Titration Apparatus, Type E.920. For zinc and cadmium coatings connection is made from the crocodile clip to the negative terminal, but for nickel it is to the positive terminal.

In order to carry out a test, the Jet Test apparatus and sample are set up in the usual manner. The potentiometer dials are adjusted to the E.M.F. corresponding to the particular plating coating, and the sensitivity dial is set at 7. The stop-cock controlling the flow of reagent is opened and simultaneously a stop-watch is started. The "magic-eye" of the titration apparatus is observed, and if it is not fully open the necessary slight adjustment of the potentiometer dial is made. On the first sign of the closing of the "magic-eye," *i.e.*, at the "penetration point," the stop-watch is stopped. The temperature of the reagent solution is then recorded.

To determine the initial setting of the potentiometer dials, preliminary tests are made, preferably with rather thick plating in order to give sufficient time to find the correct E.M.F. This setting may vary slightly with different samples of plating of a given metal, but the small adjustments can be rapidly made immediately after the start of a test. Typical values of this initial setting are: for zinc plating with number 4 solution, 830 mv.; for cadmium plating with number 3 solution, 685 mv.; and for nickel plating with F.C. solution, 200 mv.; in the sign sense previously mentioned. A further advantage of this method over the usual method requiring visual examination of the sample is that it confirms the nature of the coating as well as measuring its thickness. The initial E.M.F. will vary widely with different metals, and errors due to, for example, incorrect labelling of different types of plating are immediately apparent. Thus, with solution 3, the E.M.F. with cadmium plating is 685 mv., with zinc plating it is 860 mv., and with tin plating it is 410 mv.

This modification of the Jet Test has been compared with the standard method for several types of plating on several different base metals. The results obtained have been identical within the limits of the experimental errors. With porous plating, the measured E.M.F. has been found to change slowly as the test proceeds, but there is usually a more marked change at the "penetration point." The rate of change of the measured E.M.F. has been recorded with several types of plating. A typical example, cadmium plating on a steel base, shows a constant E.M.F. until the "penetration point," a steady fall of 250 mv. over a period of 20 seconds, and then a sensibly constant E.M.F. As the Mullard E.920 apparatus is stated to be sensitive to 2 mv., it is apparent that the proposed method for detecting the "penetration point" is capable of excellent sensitivity.

It is claimed for the proposed method that it eliminates much of the personal error inherent in the Jet Test, that it permits more rapid testing, that it provides a check on the qualitative nature of the coating, and that it is capable of greater precision than the standard method.

The author wishes to thank Mr. J. A. M. van Moll and the Directors of Philips Electrical Ltd. (formerly Philips Lamps Ltd.) for permission to publish this note.

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PHILIPS ELECTRICAL LTD.
MITCHAM JUNCTION, SURREY

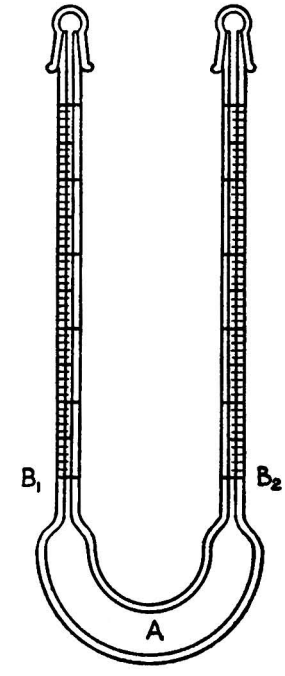
C. H. R. GENTRY
October, 1946

A PYKNOMETER WITH GRADUATED LIMBS FOR USE AT VARYING TEMPERATURES

IF the density of a liquid has to be measured accurately over a range of temperatures, it is extremely tedious to use the technique necessary with the conventional type of pyknometer, *viz.*, finding the various different weights of liquid required to fill a definite volume, because of the considerable time occupied by (i) heating to the temperature of observation, (ii) adjusting the liquid levels exactly to the marks, and (iii) cooling to balance-case temperature before each weighing. In the pyknometer now described, a quantity of liquid is weighed once and the changes of volume at various temperatures are measured. The pyknometer has two graduated limbs of capillary-tubing, in which the expansion of the liquid on raising the temperature may be observed. For very volatile liquids the saving of time with this procedure greatly reduces the possibility of errors due to evaporation.

The pyknometer is illustrated in the figure. The bulb A, in the form of a U-tube, leads at the ends into two graduated capillary tubes, which may be constructed from parts of the stem of a 1-ml. graduated pipette. The tops of the tubes may be closed by means of well fitting ground-glass caps. The presence of two openings permits easy cleaning and filling. This pyknometer differs from that of Bousfield[1] in having a graduated scale, instead of one graduation only, to each limb. Pyknometers with graduations on the limbs have been described previously,[2,3] but in these the capillary has been very fine and the graduations have been merely to facilitate setting the meniscus to a mark. In the present instrument the capillary should be wide enough to permit expansion of the liquid over the required temperature range.

For the calibration of the instrument the volume of A, up to B_1 and B_2 (the initial graduation marks), must be determined and also the accuracy of the graduations on the capillary tubes must be checked. These operations are easily performed by finding the weights of water to fill the pyknometer up to the various marks, after the scale reading has been observed in a thermostat at a suitable temperature. If graduated capillary tubing of satisfactory quality is used for the limbs, it is unlikely that any significant correction will be needed, and the only important value required in the calibration will be the volume of the bulb up to B_1 and B_2. This volume should be obtained by calibrations at a series of temperatures and a calibration curve plotted for the volume of A against temperature. Alternatively, if the coefficient of expansion of the glass is known, the variation of the volume with temperature may be calculated. This procedure is more convenient than calibration with water if the correct value of the coefficient of expansion of the glass is known, but since values for various glasses differ appreciably it is important to use an appropriate figure.



In using the instrument for the measurement of densities at a series of temperatures, a volume of liquid is introduced such that at the lowest required temperature the liquid levels are slightly above B_1 and B_2 in the capillary tubes. It is unnecessary for the levels to be adjusted to any particular mark, but the scale readings must be recorded. The pyknometer and its contents are weighed at room temperature with the caps on. It is then immersed in a bath the temperature of which can be adjusted and, after equilibrium has been reached at each temperature, the scale readings at the liquid levels are observed. By reference to the calibration curve the volume of the known weight of liquid is obtained, and hence the density is determined. The important time-saving consideration is that only one routine weighing is necessary. It may, however, be considered a desirable precaution to carry out a second weighing at the end of the series of operations to confirm that no evaporation has taken place. In our experience, evaporation is insignificant even with very volatile solvents.

The dimensions of the apparatus may be chosen according to any special requirements, but a size of general utility is from 5 to 10 ml. up to B_1 and B_2. Each capillary tube could then be about 10 cm. long and have a range of 0·5 ml. graduated in 0·01 ml. Each meniscus reading can be made with the help of a lens to about 0·001 ml. If this figure is taken as the standard deviation of the reading in each arm, then the standard deviation of the combined observations in the two arms $= [2 \times (0{\cdot}001)^2]^{\frac{1}{2}} = 0{\cdot}0014$ ml. Assuming a total volume of 10 ml., we obtain an estimate of the error in the volume measurement, expressed as a coefficient of variation, of 0·014 per cent. The possible error in the weighing may be neglected in comparison with this, so that the over-all error in the value of the density may be taken as being between 1 and 2 parts per 10,000. To obtain this accuracy, it is, of course, necessary to make the usual allowances for buoyancy in the weighing or to eliminate these by the use of a counterpoise of similar shape and suitable weight. The procedure for this is well known.[4,5,6,7]

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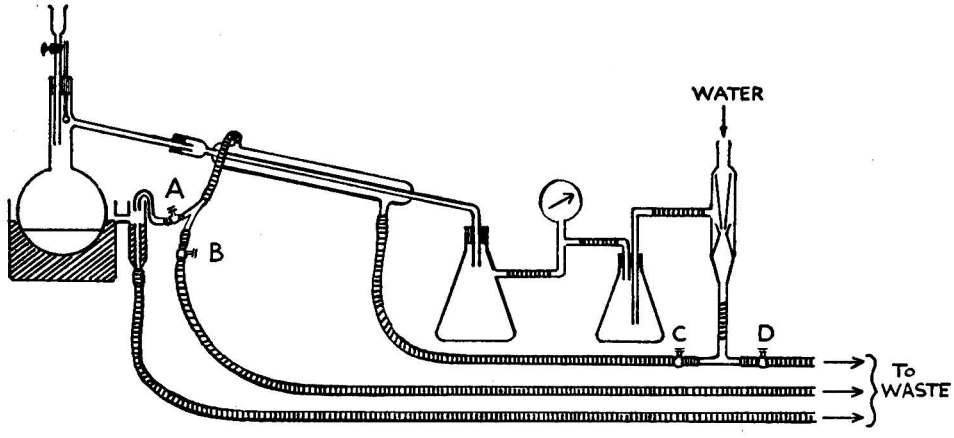
A. F. H. Ward
L. H. Brooks
Faculty of Technology
University of Manchester

June, 1947

AN ARRANGEMENT BY WHICH A SINGLE WATER TAP MAY BE USED TO RUN (*a*) A DISTILLATION *IN VACUO*, (*b*) A CONDENSER, (*c*) A CONSTANT-LEVEL WATER-BATH

In view of the present shortage of bench space, the following arrangement may be of interest to chemists as a means of effecting a considerable economy of water and space. The vacuum distillation apparatus is set up on the usual manner and consists of flask, condenser, receiver, gauge and trap connected to a water-pump. The outlet of the pump is provided with a glass T-piece to divide the stream of water into two channels controlled by screw clips C and D. Clip D regulates main outflow from the pump and hence the vacuum in the system. Clip C controls the pressure in the diverted water supply which proceeds to the condenser. The exit from the condenser is diverted by means of a glass Y-piece into two channels controlled by screw clips A and B. Clip B regulates the main outflow from the water system. Clip A regulates the

diverted water supply to the inflow for the constant-level water-bath. The outflow from the latter is to the waste as usual.



By a careful regulation of the screw clips an efficient water supply is maintained to give adequate cooling and still maintain reduced pressures of the order of −27 inches in the vacuum line with an ordinary water-pump attached to the main water supply. The manipulation is very simple and involves no additional apparatus beyond that found in most laboratories.

ENID A. M. BRADFORD
June, 1947

CAFFEINE CONTENT OF FERMENTING COFFEE EXTRACTS

THE Food Standards (Liquid Coffee Essences) Order, S.R. & O., 1945, No. 389, lays down the minimum caffeine content of liquid coffee and liquid coffee and chicory extracts. The query arose whether fermentation, frequently encountered in samples of these products, would affect the caffeine content, this being a possible though hardly credible line of defence in court proceedings.

Two weak coffee extracts, A from coffee and B from coffee and chicory, were prepared in the laboratory, both containing 20 per cent. of sugars.

When freshly prepared they yielded the following figures—

A. 0·19 per cent. (w/v) of caffeine
B. 0·15 " " "

The extracts were kept in stoppered bottles and allowed to ferment. After 12 days the fermentation had practically ceased and the specimens were again analysed, with the following results—

A. 0·18 per cent. (w/v) of caffeine
B. 0·15 " " "

The slight discrepancy in A would just be within the limits of experimental error in this determination.

PUBLIC ANALYST'S LABORATORY
PUBLIC HEALTH CENTRE
GRANGE ROAD
BERMONDSEY, LONDON, S.E.1

A. P. DAVSON
July, 1947

THE ACIDIMETRIC TITRATION OF DARK COLOURED SOLUTIONS

To the acid solution contained in a glass-stoppered cylinder, add a few drops of a dilute solution of lead acetate and a few millilitres of a solution of dithizone (50 mg. per litre) in chloroform, carbon tetrachloride, ethyl acetate, amyl alcohol, benzene or other solvent in which the dark colour is insoluble. Titrate with *N* or 0·1 *N* sodium hydroxide, shaking after each addition. The end-point is indicated by the green colour of the dithizone changing to the red of the lead dithizone compound.

The colour-change takes place at about the same *p*H value as that of methyl orange. This method cannot, therefore, be used for the titration of weak acids.

For help and advice in preparing this and the following notes and for permission to publish, I wish to thank the Government Chemist, Mr. G. W. Baker.

DEPARTMENT OF HEALTH
GOVERNMENT CENTRAL LABORATORIES
JERUSALEM

W. HIRSCH
January, 1947

A PERMANENT STANDARD FOR ESTIMATION OF CHOLESTEROL

A PERMANENT standard for the colorimetric estimation of cholesterol, which has very nearly the same green tint as that given by the Lieberman reaction, may be prepared by mixing 10 ml. of a 10 per cent. solution of nickel sulphate ($NiSO_4$, $7H_2O$), 10 ml. of 0·1 *N* sulphuric acid and 0·9 ml. of a 10 per cent. solution of ferric chloride ($FeCl_3$, anhydrous).

DEPARTMENT OF HEALTH
GOVERNMENT CENTRAL LABORATORIES
JERUSALEM

W. HIRSCH
January, 1947

ALBUMIN IN SERUM

WHEN the digested solutions obtained by Hawk and Bergeim's method are treated with Nessler's reagent, a turbidity appears with many samples. This makes an accurate colour match impossible.

The difficulty was overcome by taking five times the usual quantities and diluting before adding Nessler's reagent.

Method—Take 5 ml. (instead of 1·0 ml.) of the filtrate after separation of the globulin, digest and make up to 100 ml. in a measuring cylinder, allow to settle and pipette 20 ml. for the nesslerisation. It would appear that the turbidity is caused by traces of silica dissolved from the glass during the digestion and that the subsequent dilution and settling practically removes the interference.

REFERENCES

Hawk and Bergeim, "*Practical Physiological Chemistry*," 11th Ed., 1938, Churchill Ltd., London.
Beaumont and Dodds, "*Recent Advances in Medicine*," 11th Ed., 1943, Churchill Ltd., London.

DEPARTMENT OF HEALTH
GOVERNMENT CENTRAL LABORATORIES
JERUSALEM

W. HIRSCH
January, 1947

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Health since the last record in THE ANALYST (1947, **72**, 543).

Public Analyst	*Appointments*
CREGEEN, William Allan (Deputy)	County Borough of Leicester.
DALLEY, Richard Arthur (Deputy)	County of Somerset.
HERON, Neil (Additional)	County Boroughs of Liverpool, Southport, Bootle, Blackburn, Birkenhead and Barrow-in-Furness. Boroughs of Crosby and Widnes.
ROBERTS, Miss Muriel (Additional)	County Boroughs of Liverpool, Southport, Bootle, Blackburn, Birkenhead and Barrow-in-Furness. Boroughs of Crosby and Widnes.
TAYLOR, William Wilders	Kesteven County Council and Lindsey County Council.

British Standards Institution

A FEW copies of the following draft Specifications, issued for comment only, are available to interested members of the Society and may be obtained on application to the Secretary, J. H. Lane, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee PVC/3—Oils, Varnishes, Putty, etc.
CJ(PVC)5273—Draft for Tung Oil (Revision of B.S.391).

Draft Specification prepared by Sub-Committee CEB/6/4—Concrete Flags and Kerbs.
CJ(CEB)5279—Draft for Pre-cast Concrete Kerbs, Channels, Edgings and Quadrants (Revision of B.S.340).

Draft Specification prepared by Technical Committee DAC/5—Sampling of Dairy Products.
CJ(DAC)5086—Draft for the Sampling of Dairy Products (Revision of B.S.809).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Preparation of Ash and Spectrochemical Determination of Traces of Metallic Elements in Oils, Fats, and Related Substances. R. T. O'Connor, D. C. Heinzelman, and M. E. Jefferson (*J. Amer. Oil Chemists Soc.*, 1947, **24**, 185–189)—Traces of metals adversely affect the keeping qualities of refined fats and oils; the amount of ash and, consequently, of any metals is very small. The authors have devised a special method of ashing designed to recover the metals completely. These are then determined spectrochemically.

Procedure—Weigh accurately 2·5 g. of the oil or fat into a silica dish, add 5 ml. of an alcoholic solution of magnesium nitrate (250 g. of $Mg(NO_3)_2.6H_2O$ per litre of 95 per cent. ethanol), and cover with an inverted glass funnel. Heat on an electric hot-plate, gradually raising the temperature until fumes are given off. Maintain at this temperature as long as fuming continues, then slowly raise to about 300° C., and continue heating for 30 min. Cool the sample, add 1 ml. of an internal-standard solution, and dry overnight in a vacuum desiccator over phosphorus pentoxide. Ash in a muffle furnace at an initial temperature of 225° C. and raise the temperature by 25° C. at 30-min. intervals until 450° C. is reached. Maintain at 450° C. overnight, cool, transfer to a mortar, grind finely, and preserve in a stoppered bottle.

Porcelain dishes must not be used as they contaminate the ash with copper, aluminium, and iron. A suitable internal standard for the determination of aluminium, copper, iron, nickel, and manganese is an aqueous solution containing 0·1 g. of germanium dioxide and 15 ml. of concentrated hydrochloric acid per litre; for the estimation of tin and zinc, an aqueous solution containing 3·312 g. of lead nitrate per litre gives good results.

This method, in effect, reduces the spectrochemical analysis to the determination of impurities in magnesium oxide. To obtain standard curves, samples of a molecularly distilled oil are ashed as described, and it must be shown that they and the magnesium nitrate are free from contaminants. Similarly, it must be shown that the internal-standard solutions contain no traces of the elements to be determined. Standards for each element to be estimated are prepared by addition of graded amounts of a solution of the element, varying from 0·0001 to 0·4 per cent. as the metal (based on the 2·5 g. sample), to a series of 2·5-g. samples of molecularly distilled oil.

Spectrograms are made on exactly 5-mg. samples of the ash, contained in a cup in the pure carbon positive electrode. The best results are obtained with direct current at 235 v. and 20 amp., but the heat generated makes water-cooling of the electrode holders necessary. A. H. A. ABBOTT

Determination of Acetanilide in the Presence of Caffeine. E. D. Robinson and S. C. Werch (*J. Amer. Pharm. Assoc., Sci. Ed.*, 1947, **36**, 185–187)—*Procedure*—Place either a whole weighed tablet or a suitable weighed portion of powder in a small evaporating dish and digest on a water-bath for 2·5 hr. with 10 ml. of 10 per cent. sulphuric acid, adding water from time to time to keep the volume greater than 5 ml. Transfer the digested material to a Gooch crucible, filter under reduced pressure, wash the residue well with water, and transfer the filtrate and washings to a separating funnel. Extract the caffeine with four 25-ml. quantities of chloroform, evaporate the chloroform in a small flask, and weigh the residue as anhydrous caffeine. Gently warm the extracted liquid to remove chloroform, transfer to a glass-stoppered flask, add 50·0 ml. of standardised 0·1 *N* potassium bromate - bromide, 5 ml. of concentrated hydrochloric acid, and a few crystals of potassium iodide. Set aside for 5 min. and titrate back with 0·1 *N* sodium thiosulphate in presence of starch as indicator. One ml. of 0·1 *N* potassium bromate - bromide is equivalent to 0·00433 g. of acetanilide.

Recoveries averaging 99·8 per cent. of acetanilide were obtained by this rapid method.

A. H. A. ABBOTT

Spectrophotometric Studies of the Roe Method for the Determination of Dehydroascorbic Acid. R. A. Bolomey and A. R. Kemmerer (*J. Biol. Chem.*, 1947, **167**, 781–785)—The method of Roe (*J. Biol. Chem.*, 1943, **147**, 399; 1944, **152**, 511; ANALYST, 1943, **68**, 260) depends on the formation of a red coloration by the action of 85 per cent. sulphuric acid on the 2 : 4-dinitrophenylhydrazone of dehydroascorbic acid; ascorbic acid is estimated by prior oxidation.

The use of glacial acetic acid as solvent for the dinitrophenylhydrazone instead of 85 per cent. sulphuric acid has been investigated. The derivative obtained from pure dehydroascorbic acid has an absorption maximum at 510 to 520 mμ. in both solvents, but the extinction coefficient in acetic acid is about 1·3-fold that in sulphuric acid. In the estimation of the ascorbic acid content of citrus juices, the method of oxidation and the solvent used determine the shape of the absorption curve; additional absorption, mainly at wavelengths shorter than 520 mμ., is produced. This distortion of the spectrum appears to be due to substances readily oxidisable to products that react with dinitrophenylhydrazine, and depends on the nature of the sample and its treatment. In the estimation of ascorbic acid in citrus juices, it is possible in certain instances, by taking the difference between the absorption curves of the dinitrophenylhydrazones of the oxidised and unoxidised material, to obtain a curve identical with that derived from dehydroascorbic acid. In other instances, marked deviations occur at

wave-lengths shorter than 520 mμ. It is essential to carry out a blank determination on the unoxidised material when estimating ascorbic acid by the Roe method. It is concluded that sulphuric acid provides a better differentiation of the various maxima in the absorption curves, but that when a spectrophotometer of narrow slit width is available glacial acetic acid is to be preferred as solvent.

The method of Penney and Zilva (*Biochem. J.*, 1945, **39**, 392; ANALYST, 1946, **71**, 242), which depends on the difference in the rates of formation of the dinitrophenylhydrazones of dehydroascorbic acid, and of reductones, is criticised on the grounds that the conditions of time and temperature are too critical. G. H. TWIGG

Biochemical

Estimation of Dienoestrol. M. B. Sahasrabudhe and A. E. W. Smith (*Biochem. J.*, 1947, **41**, 190–192)—Dienoestrol reacts with maleic anhydride to give an adduct soluble in aqueous sodium bicarbonate solution. Other substances soluble in bicarbonate are formed from other conjugated dienes and from alcohols but, in practice, the method gives only small blanks with urine containing no dienoestrol. These small errors can be eliminated by steam-distilling the solution containing the adduct. When only small amounts of dienoestrol are present, a colorimetric procedure is used.

Procedure—Hydrolyse 1 to 2 litres of urine by heating under refluxing conditions for 10 min. after the addition of 100 ml. of concentrated hydrochloric acid per litre. Extract in a continuous extractor with benzene for 24 hr. and distil the benzene extract from an oil-bath after adding 10 ml. of anisole. After removal of the benzene, make up the volume of the residue to 15 ml. with anisole, and shake the solution for 1 to 5 min. with 15 ml. of 10 per cent. sodium carbonate solution. Discard the aqueous layer and repeat the extraction five to seven times until less than 0·5 mg. of acid is extracted by the carbonate solution from the anisole layer. Add 1·0 g. of solid maleic anhydride to the anisole solution and shake overnight at room temperature. Remove the excess maleic anhydride by shaking with five or six 15-ml. portions of water until no further acidic material is extracted. Shake the anisole solution overnight with 15 ml. of saturated, aqueous sodium bicarbonate solution and with two further 15-ml. portions for 2 hr. each. Acidify the combined bicarbonate layers with dilute hydrochloric acid to congo red, steam-distil for 30 min., and then extract the residue with ether. Dry the extract over sodium sulphate, evaporate the solution, and dry and weigh the residue. This method gives recoveries of 60 to 70 per cent. with amounts of dienoestrol ranging from 3 to 20 mg. per litre. With amounts smaller than this, high blanks are obtained and the dienoestrol must then be estimated by coupling with diazotised sulphanilic acid and evaluating the red colour thus formed. Dissolve the residue in 5 ml. of 2 *N* sodium hydroxide and mix 1 ml. with 2 ml. of diazotised sulphanilic acid (dissolve 1·0 g. of sulphanilic acid in 8·0 ml. of *N* sodium hydroxide, add 50 ml. of water, followed by 7·0 ml. of 36 per cent. hydrochloric acid, and cool to 0° C.; add 8·0 ml. of 10 per cent. sodium nitrite solution at 0° C., and dilute to 100 ml. with water). After 5 min. at room temperature, dilute with 10 ml. of *N* sodium hydroxide and, 5 min. later, evaluate the colour in a Spekker absorptiometer. Calculate the results from a graph prepared from solutions containing known amounts of adduct.

F. A. ROBINSON

Organic

Capillary Method in Qualitative Analysis. A. A. Korinfsky (*Zavod. Lab.*, 1945, **11**, 541–542)—A method for increasing the sensitivity of colour reactions is described. The coloured complex is dissolved in ether, and the ether solution is drawn up by capillary attraction through a narrow band of filter paper, enclosed, except for the upper end, in a glass tube. Evaporation of the ether thus occurs only at the end of the filter paper and the coloured compound becomes concentrated at this point, enabling very small amounts to be detected.

Procedure—In an ordinary test tube with a well-fitting cork carrying a glass tube, 5 to 6 cm. long and 4 mm. in internal diameter, place the solution being tested, together with the appropriate reagent, so that the test tube is about two-thirds filled. Introduce 2 ml. of ether, shake well, close the test tube and insert a strip of filter paper into the narrow tube so that it dips 3 or 4 mm. into the ether, and fold it at the other end so that it does not fall through the tube. Examine the outer end of the filter paper after a few minutes (in rare cases, after 30 to 40 min.).

Sensitivity—In the following list, after the name of the ion to be tested for, are given the name of the reagent used, the coloration obtained on the paper, and the limiting concentration, the last being approximately defined by the minimum concentration that can be detected under the above-mentioned conditions in 1 hr.: $Fe^{\cdots}$, ammonium thiocyanate, reddish-brown, 1 in 30,000,000; VO_3', 8-hydroxyquinoline, violet, 1 in 20,000,000; $Cu^{\cdot\cdot}$, diphenylcarbazide, reddish-violet, 1 in 100,000,000; NO_2', quinol, violet, 1 in 20,000,000; Br', fluorescein, red, 1 in 1,000,000; I', starch, violet, 1 in 20,000,000. In tests on bromide, bromine is liberated and extracted by the ether and is drawn up a filter paper, the end of which has been treated with 1 drop of 0·1 per cent. fluorescein solution and then dried. Similarly, with iodide the end of the paper has been treated previously with starch (1 per cent.) and potassium iodide (0·05 per cent.) solution; this test is carried out in the dark.

Since all "ashless" filter paper appears to contain sufficient iron to interfere with the detection of small amounts of iron and other elements, the paper is pre-treated as follows. Dip one end of a strip of filter paper into 1 per cent. hydrochloric acid, leave for 1 hr., then cut a piece off the upper end, dry the remainder, and dip it into ether. After 10 min., cut a piece off the upper end (the iron will have become concentrated here); the paper is then ready for use.

Water should be examined particularly for the presence of copper, and the purity of the reagents used should be established. G. S. SMITH

4-Chloro-2-aminophenol-5- and -6-sulphonic acids, their Characterisation and Differentiation. J. F. Gaunt, the late F. M. Rowe, and J. B. Speakman (*J. Soc. Dyers and Col.*, 1947, **63**, 48–51)—The similarity between the properties of the pairs of dyes made by coupling diazotised 4-chloro-2-aminophenol-5- and -6-sulphonic acids is so close that the identity of the former compound was open to suspicion, the identity of the latter compound being well established. The authors have prepared the -5-sulphonic acid and have characterised the two compounds by conversion to oxazolone derivatives and preparation of the *S*-benzylthiuronium salts and the *p*-toluidine salts of the latter.

Preparation of 4-chloro-2-aminophenol-5-sulphonic acid—Heat gently under reflux 260 g. of 4-chloro-2-nitrophenol with 800 ml. of concentrated hydrochloric acid and add 265 g. of granulated tin in small portions during 1 hr. Boil for 1 hr. longer, filter, and concentrate the filtrate to 400 ml. Add 400 ml. of concentrated hydrochloric acid, whereupon long colourless needles are deposited. On recrystallisation from 20 per cent. hydrochloric acid, 199 g. (73·7 per cent.) of 4-chloro-2-aminophenol hydrochloride are obtained as colourless needles. *5-Chlorobenzoxazolone*—Mix 180 g. of 4-chloro-2-aminophenol hydrochloride with 150 g. of urea in a porcelain dish and heat gently until molten. Heat the molten mixture for a further 35 min. Dissolve the cold melt in alcohol (750 ml.; charcoal), filter, and add the filtrate to 2 litres of cold, 5 per cent. hydrochloric acid, whereupon 5-chlorobenzoxazolone (97 g.; 57·4 per cent.) separates as pale fawn needles, m.p. 188° C.

5-Chlorobenzoxazolone-6-sulphonic acid—Dissolve 85 g. of 5-chlorobenzoxazolone, dried by heating at 105° C. for 5 hr., in 250 g. of "monohydrate" and heat the solution to 80° C. Add 340 g. of 12 per cent. oleum during 1 hr., with good stirring, and maintain the mixture at 80° C. for 10 hr. Pour the cold reaction mixture into 5 litres of water, heat to boiling, and neutralise to Congo red by adding powdered calcium carbonate. Remove calcium sulphate from the boiling solution by filtration, extract with five portions of 2 litres each of boiling water, and add 80 g. of sodium hydroxide to the combined filtrate and washings, which are then concentrated to 1 litre. Filter, and add 300 ml. of concentrated hydrochloric acid to the hot filtrate. On cooling, 88 g. (71·7 per cent.) of sodium 4-chloro-2-aminophenol-5-sulphonate are obtained as colourless, prismatic crystals.

p-*Toluidine salt of diacetyl-4-chloro-2-aminophenol-5-sulphonic acid*—Grind 2 g. of sodium 4-chloro-2-aminophenol-5-sulphonate with 1·2 ml. of pyridine. Add 2·5 ml. of acetic anhydride and stir for 10 min. Add 3 ml. of alcohol, whereupon the pyridine salt of the diacetyl chloroaminophenol sulphonic acid separates; on recrystallisation from alcohol, colourless crystals, which do not melt below 340° C., are obtained. Thus, pyridine is lost during recrystallisation and the product is sodium diacetyl-4-chloro-2-aminophenol-5-sulphonate. Further, add the acetylation mixture to 10 ml. of distilled water, boil, and add 1·1 g. of *p*-toluidine dissolved in 6 ml. of boiling 20 per cent. hydrochloric acid. The *p*-toluidine salt of diacetyl-4-chloro-2-aminophenol-5-sulphonic acid crystallises from water in colourless plates, m.p. 143° to 144° C.

p-*Toluidine salt of diacetyl-4-chloro-2-aminophenol-6-sulphonic acid*—This is prepared in the same way, and forms colourless plates, m.p. 135° to 136° C.

5-Chlorobenzoxazolone-6-sulphonic acid—Pass phosgene at 5° C. into a solution of 11·2 g. of 4-chloro-2-aminophenol-5-sulphonic acid in 40 ml. of water containing 6 g. of sodium hydroxide until the solution is no longer alkaline to phenolphthalein. The precipitated sodium 5-chlorobenzoxazolone-6-sulphonate crystallises from water in colourless plates; yield 9·1 g. = 66·8 per cent.

S-*Benzylthiuronium salt of 5-chlorobenzoxazolone-6-sulphonic acid*—Add a solution of 2·2 g. of *S*-benzylthiuronium chloride in 10 ml. of water to a solution of 2·7 g. of sodium 5-chlorobenzoxazolone-6-sulphonate in 25 ml. of water and cool the mixture to 5° C. The colourless crystalline precipitate crystallises from 50 per cent. alcohol in hexagonal plates, m.p. 242° C. (3·1 g.; 74·6 per cent.).

p-*Toluidine salt of 5-chlorobenzoxazolone-6-sulphonic acid*—Add a solution of 1·2 g. of *p*-toluidine in 6 ml. of 20 per cent. hydrochloric acid to a boiling solution of 2·7 g. of sodium 5-chlorobenzoxazole-6-sulphonate in 20 ml. of water. Cool, and recrystallise the *p*-toluidine salt from water, whereupon it forms pale lemon-yellow crystals, m.p. 268° to 269° C. (2·8 g.; 78·5 per cent.).

5-Chlorobenzoxazolone-7-sulphonic acid—Prepare from 4-chloro-2-aminophenol-6-sulphonic acid in the same way as 5-chlorobenzoxazolone-6-sulphonic acid. It crystallises from water in colourless needles.

S-*Benzylthiuronium salt of 5-chlorobenzoxazolone-7-sulphonic acid*—Prepare in the same way as the salt of the -6-sulphonic acid. Recrystallise from 50 per cent. alcohol to form colourless plates, m.p. 220° C.

p-*Toluidine salt of 5-chlorobenzoxazolone-7-sulphonic acid*—Prepare in the same way as the salt of the -6-sulphonic acid. It crystallises from water in colourless needles, m.p. 284° C.

2-Aminophenol-5-sulphonic acid—Evaporate 80 g. of *o*-aminophenol to dryness on a steam-bath with 100 ml. of concentrated hydrochloric acid, and gently heat the hydrochloride obtained with 80 g. of urea; continue the heating until evolution of ammonia ceases. Dissolve the cold mixture in 750 ml. of boiling, 10 per cent. hydrochloric acid; benzoxazolone crystallises in pale bluish-grey needles, m.p. 137° to 138° C. (52 g.; 52·5 per cent.). Sulphonate benzoxazolone by dissolving 50 g. of benzoxazolone in 85 g. of "monohydrate" at 5° to 10° C. and adding 55 g. of 65 per cent. oleum at that temperature during 1 hr. Stir for 6 hr. and complete the reaction by maintaining the vessel at room temperature for 36 hr. Pour the sulphonation mixture into 250 g. of chopped ice, heat to boiling, and neutralise with milk of lime.

Filter, wash the calcium sulphate, add sodium carbonate to the combined filtrate and washings, and filter off the precipitated calcium carbonate. Add 35 g. of sodium hydroxide to the filtrate and heat the mixture under refluxing conditions for 5 hr. Neutralise the cold solution to Congo red by adding concentrated hydrochloric acid; further addition of 50 ml. of concentrated hydrochloric acid results in crystallisation of 2-aminophenol-5-sulphonic acid as colourless needles (39 g.; 54 per cent.).

Benzoxazolone-6-sulphonic acid—Prepare from 2-aminophenol-5-sulphonic acid in the same manner as 5-chlorobenzoxazolone-6-sulphonic acid. Crystallise sodium benzoxazolone-6-sulphonate from water in colourless needles.

S-*Benzylthiuronium salt of benzoxazolone-6-sulphonic acid*—Prepare in the same manner as the *S*-benzylthiuronium salt of 5-chlorobenzoxazolone-6-sulphonic acid and crystallise from 50 per cent. alcohol in colourless plates, m.p. 235° C.

p-*Toluidine salt of benzoxazolone-6-sulphonic acid*—Prepare in the same manner as the *p*-toluidine salt of 5-chlorobenzoxazolone-6-sulphonic acid and crystallise from water in colourless needles, m.p. 256° to 257° C.

Benzoxazolone-5-sulphonic acid—Prepare from 2-aminophenol-4-sulphonic acid in the same manner as the -6-sulphonic acid. Crystallise sodium benzoxazolone-5-sulphonate from water in colourless plates.

S-*Benzylthiuronium salt of benzoxazolone-5-sulphonic acid*—Prepare in the same manner as the *S*-benzylthiuronium salt of 5-chlorobenzoxazolone-6-sulphonic acid and crystallise from 50 per cent. alcohol in colourless plates, m.p. 198° C.

p-*Toluidine salt of benzoxazolone-5-sulphonic acid*—Prepare in the same manner as the *p*-toluidine salt of 5-chlorobenzoxazolone-6-sulphonic acid and crystallise from water in colourless needles, m.p. 249° to 250° C. E. M. POPE

Determination of the Content of Pyridine Bases in Products containing Ammonia or Ammonium Salts. M. E. Neymark (*Zavod. Lab.*, 1946, **12**, 551–552)—The distillation method, in which ammonia is destroyed by hypobromite, is criticised on the ground that the *p*H of the solution in the distillation flask is too low for quantitative recovery of the pyridine bases. Buffering of the solution at about *p*H 4 is recommended, and distillation can be carried out without the use of bromine.

Procedure—Dilute the sample, containing about 0·15 g. of pyridine bases, to 150 to 200 ml. with water, make the solution alkaline to phenolphthalein, and distil off the pyridine bases and ammonia from a Kjeldahl flask into a receiver containing 10 ml. of 10 per cent. sulphuric acid and 10 drops of mixed indicator (0·05 per cent. of dimethyl yellow and 0·05 per cent. of methylene blue in alcohol) until about one-half the contents of the flask has passed over. Neutralise the distillate, transfer it to a Kjeldahl flask, add 20 ml. of saturated sodium dihydrogen phosphate solution, and distil into 30 ml. of 0·1 *N* sulphuric acid, containing the mixed indicator. The pyridine bases, free from ammonia, are thus collected. Titrate back with 0·1 *N* alkali free from carbonate, and calculate the content of pyridine bases on the assumption that they have an equivalent weight of 100. G. S. SMITH

Decomposition and Analysis of Organic Compounds containing Fluorine and Other Halogens. J. F. Miller, H. Hunt, and E. T. McBee (*Anal. Chem.*, 1947, **19**, 148–149)—*Decomposition of sample*—Weigh gaseous samples, or liquids boiling below 50° C., in closed Pyrex vials made by first sealing one end of drawn-out 7-mm. tubing, and then the other after drawing in the sample by alternate heating and cooling of the vial. For less volatile samples, use glass-stoppered Victor Meyer weighing vials, open vials, or small porcelain micro-combustion boats, according to the volatility and viscosity of the sample. Put the vessel containing between 0·002 and 0·120 g. of the sample into a reaction tube (a 50-cm. length of 13- to 14-mm. Pyrex tubing, sealed at one end) with 5 ml. of dry ether. Add 0·5 to 1·0 g. of sodium in small pieces, and place the tube in a dry-ice - alcohol cooling-bath. Distil between 10 and 15 ml. of liquid ammonia into the tube, seal as for a Carius tube, and shake at room temperature for at least 5 hr.; a machine constructed to rotate the tube end-over-end at 12 r.p.m. is suitable. When decomposition is complete, cool in a dry-ice - alcohol bath, and release the slight pressure in the tube by applying a small flame near the seal. Break off the tip and put it into a 500-ml. Erlenmeyer flask containing 10 ml. of 95 per cent. ethanol, then remove the tube from the bath and, after wiping it, invert it into the flask. When the vigorous reaction subsides, rinse the tube with small quantities of ethanol and hot distilled water, the washings, which should not exceed 150 ml., being collected in the flask. If carbonisation occurs, filter the solution through a sintered funnel.

In handling the reaction tubes and liquid ammonia, safety equipment should be used.

Determination of fluoride—Transfer the filtered solution to a volumetric flask and dilute accurately to 250 ml. Acidify 100 ml. in a 500-ml. Erlenmeyer flask with nitric acid and determine the halide, other than fluoride, by the modified Volhard method, nitrobenzene being used to coagulate, coat, and remove the silver halide from the reaction medium.

Transfer another 100-ml. aliquot portion to a 400-ml. beaker, and treat with diluted hydrochloric acid (100 ml. of C.P. acid diluted to 1 litre) according to the fluoride content of the sample. If the fluorine content is not known to within 5 per cent., treat first as for a 50 per cent. content, and repeat the determination calculating from the first result. Make corrections to allow for the chloride ions furnished by the sample, so that concentrations as shown in the Table can be established. Then neutralise the solution to methyl orange using diluted (1 + 3) nitric acid, and add 3 drops in excess. Cool the solution to 5° ± 1° C., add 15 ml. of 10 per cent. lead acetate solution containing 80 ml. of glacial acetic acid per litre, and cool at

that temperature for 1 hr. with frequent stirring. Filter, and wash the precipitate three or four times with cold water, dissolve in diluted (1 + 3) nitric acid, and titrate the chloride ions present by the Volhard method. The fluorine concentration is calculated from the formula PbClF.

VOLUME OF DILUTED HYDROCHLORIC ACID SOLUTION FOR 0·12-G. SAMPLES CONTAINING DIFFERENT PERCENTAGES OF FLUORINE

F %	HCl ml.	F %	HCl ml.	F %	HCl ml.
5	3·80	35	1·79	70	2·43
10	3·23	40	1·90	75	2·59
15	2·68	45	1·96	80	2·75
20	2·18	50	2·02	85	2·91
25	1·95	55	2·09		
30	1·77	60	2·16		
31·5	1·73	65	2·27		

At 31·5 per cent. of F, the minimum quantity of chloride ion is required.

Results—The method gives complete decomposition, and the fluorine determination is as accurate as any known method, and considerably quicker. The greatest deviation on fluorine values is 1 in 64, although four of the six results given are better than 1 in 400. The maximum deviation of the means of chlorine determinations from the theoretical is 1 part in 62, four compounds being analysed.

Research materials containing bromine and iodine were satisfactorily analysed by the same method, but no standard materials were available.

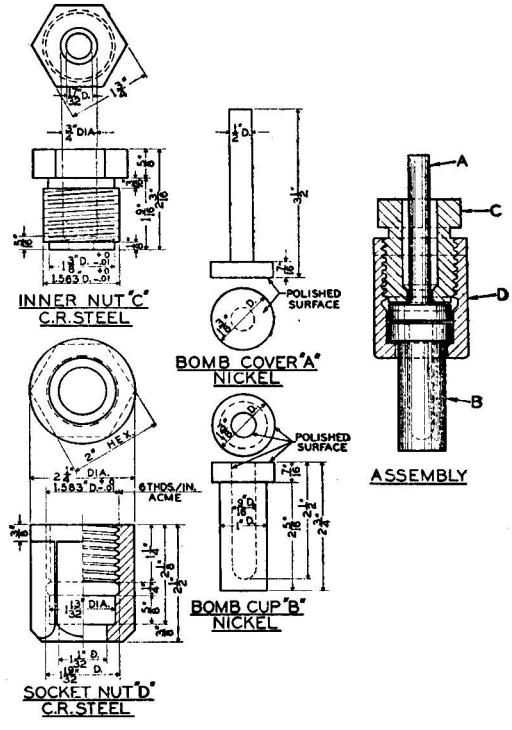
M. E. DALZIEL

Determination of Fluorine and Chlorine in Organic Compounds. R. H. Kimball and L. E. Tufts (*Anal. Chem.*, 1947, **19**, 150–153)—Heating with potassium does not always attack fluorine-containing organic compounds quantitatively, and when specially resistant glass is used to allow prolonged reaction, high results are obtained, possibly because of extraction of fluorine from the glass. Using the nickel bomb described, and heating at 500° to 550° C. for 2 hr., complete attack is effected, and a clear solution is obtained for the subsequent determinations.

Procedure—Decomposition of sample—Before use, the steel parts, C and D, of a new bomb must be slowly heated in a muffle until covered with a blue oxide coating. Lubricate the nickel-steel interfaces with high-temperature grease and graphite, and seal the bomb by means of a 1·875-in. circle of heavy cellophane, which carbonises as the temperature rises. When charged, assemble the bomb to finger-tightness, and hold D, the steel socket nut, in a vice and tighten the inner nut, C, with a wrench. When opening, loosen C a part-turn, and tap A and B gently to break the seal and release the pressure before removing C and D.

Solids and liquids should be weighed into gelatin capsules, more volatile liquids into thin glass ampoules, and gases into an ampoule bulb blown in the middle of a capillary tube, cooled to condense a suitable amount of the sample. The sample weight should vary from 0·10 g. for high fluorine contents to 0·35 g. for low fluorine contents.

Clean and dry the bomb, and put into B pieces of potassium metal totalling 1 g. in weight. Add the weighed sample and ampoule, insert the cellophane circle, and close and tighten the bomb. Heat in a muffle at 500° to 550° C. for 2 hr., keeping the bomb slanted and avoiding contact of the potassium with the gasket. Remove and cool the bomb, open it as described, keeping the cover, A, on the cup, B. Place 10 ml. of methanol, redistilled until free from chloride, in a Pyrex tube, 17 cm. × 5 cm., and close the top with a bung bearing a 40-cm. reflux condenser. Replace the air with carbon dioxide through a tube extending down to 1 in. below the condenser. Remove the bung and condenser, and lower A and B into place,

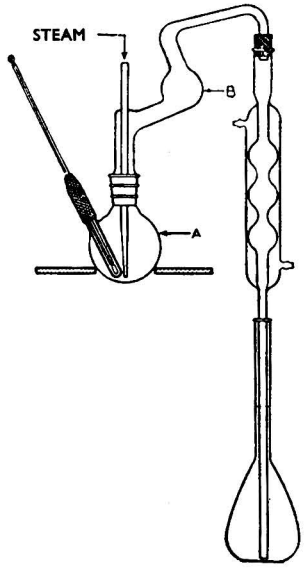


remove A, and replace the condenser. Purge briefly with carbon dioxide, remove the tube, and heat on a steam-bath until the methanol refluxes rapidly, to decompose the excess of potassium. After 10 min., break any lumps with a long rod, and after a further 10 min., remove the rod, rinsing it with 20 ml. of water. Continue the heating for 15 min.

Wash A, B, and the refluxing apparatus with warm water, and collect the liquid, and any carbon adhering to the sides of the bomb, in a 500-ml. Erlenmeyer flask. To the 200 to 250 ml. of liquid collected, add 1·5 g. of ammonium bicarbonate and some boiling beads, and concentrate to 75 to 100 ml. to remove methanol and the hydrocyanic acid formed from the gelatin, to convert the potassium hydroxide to carbonate, and to complete the extraction of fluorine and chlorine from the

carbonaceous residue. Filter the solution into a flask calibrated to hold 203 ml., wash the residue well and dilute the clear solution and washings to 203 ml.

Distillation—Using a steam distillation apparatus of the design shown, pass steam from a source containing 1 or 2 g. of potassium permanganate and some soft glass beads into the Pyrex flask, A, of 250-ml. capacity with a thermometer well containing mercury and a ground-glass joint. The distilling head, B, minimises the liquid splashing over, and the 3-bulb condenser dips into a 500-ml. volumetric flask. A is heated through a 2·25-in. hole in a Transite board.



Standardisation of thorium nitrate solution—Prepare a solution of sodium fluoride containing 1·0000 g. of fluoride ion per litre. Take a 50-ml. portion, dilute it with water to 100 ml. in A, add 8 to 10 beads, and 0·5 g. of ground glass. Put 5 ml. of 5 per cent. sodium bicarbonate solution in the receiver. Add 25 ml. of 72 per cent. perchloric acid and 1 ml. of 33 per cent. silver perchlorate to A, and set B in position. Connect the steam supply, and concentrate the sample solution over a strong flame until a temperature between 128° and 132° C. is reached. Maintain the temperature until 440 to 470 ml. are collected, by varying the steam current. Stop the distillation, remove and rinse the condenser, and dilute the distillate and washings to 500 ml.

Pipette 50 ml. of the solution into a 125-ml. flask, add 1 ml. of 0·01 per cent. aqueous sodium alizarin sulphonate, and just sufficient 0·5 *N* nitric acid barely to produce a yellow coloration. Add 1 ml. of a buffer solution prepared by dissolving 9·4 g. of chloroacetic acid in 30 ml. of water, diluting to 60 ml., neutralising 38 ml. with 20 per cent. sodium hydroxide solution, mixing this neutralised portion with the remainder, and diluting to 100 ml. The buffer solution is stable for 2 weeks. Titrate the solution with standard thorium nitrate solution (containing 2·0 g. of the tetrahydrate in a litre of 0·01 *N* nitric acid), added dropwise, and not more quickly than 5 ml. per min. Swirl continuously to the appearance of a permanent pink coloration, as compared with a blank.

To prepare a blank solution, dilute a portion of the standard solution five-fold, and pipette 20 ml. (containing 4 mg. of fluoride ion) into a 125-ml. flask, add 30 ml. of water, 1 ml. of indicator, and 1 ml. of the buffer solution. Run in slowly 12·5 ml. of thorium nitrate, and compare in fluorescent light on white paper, the solutions being alike until equivalence is reached. The titration should not take longer than 10 to 15 min., and the thorium fluoride which settles out should be pink after several hours' standing.

Titrate a similar solution containing 1 mg. of fluoride ion. The blank correction is determined as follows,

Let A = ml. equivalent to 5 mg. of F′ + titration blank

Let B = ml. equivalent to 1 mg. of F′ + titration blank

Then $(A - B)$ = ml. equivalent to 4 mg. of F′

$(A - B)/4$ = ml. equivalent to 1 mg. of F′ = C

$B - C$ = ml. equivalent to titration blank

$5/(A$ − titration blank) = mg. of fluoride ion per ml. of thorium nitrate solution

Standardisation without the distillation gives higher results owing to incomplete recovery of the fluoride, a constant fraction of which, 0·8 per cent., escapes distillation.

Determination of fluoride—To determine the fluorine in the unknown solution obtained by decomposition of the sample as described above, pipette 100 ml. into flask A; a smaller portion should be used if more than 70 mg. of fluoride ion are present. Add 10 drops of 5 per cent. potassium permanganate solution, and heat on the steam-bath for 1 hr.; add a few more drops of permanganate solution to maintain the colour if necessary. Add 0·5 g. of ferrous sulphate to reduce the excess of permanganate and to prevent the liberation of free chlorine and, while still hot, add 8 to 10 beads, 0·5 g. of ground glass, and 2 ml. of 33 per cent. silver perchlorate solution for each 100 mg. of chlorine likely to be present. Add 5 ml. of 5 per cent. sodium bicarbonate solution to the receiver, and 25 ml. of 72 per cent. perchloric acid. Connect to the steam supply and begin the distillation immediately. Titrate the distillate in a volume of 50 ml. containing 2 to 6 mg. of fluoride. Determine a blank on the reagents as described for chlorine.

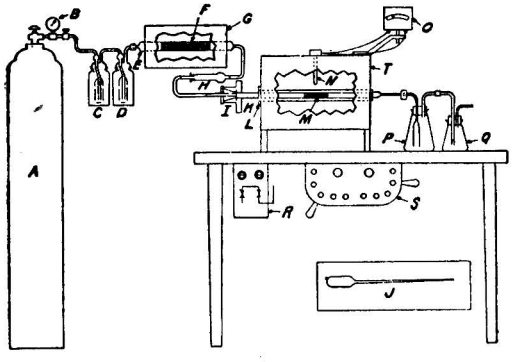
Determination of chlorine—Take 100 ml. of the solution obtained from the decomposition of the sample in a 500-ml., glass-stoppered Erlenmeyer flask, and heat as above with some potassium permanganate. After 1 hr., add dilute hydrogen peroxide dropwise to reduce the excess of permanganate. Acidify with nitric acid, and add more peroxide to dissolve any manganese dioxide formed. Cool, and titrate the chloride by the Volhard method.

Determine a blank on the capsule and reagents by running a complete experiment, using only an

empty capsule in the bomb. Titrate in the same volume as the determination. In the absence of fluoride the thorium nitrate solution shows no blank, but in its presence there is a definite blank which must be determined as described.

The results obtained for the fluorine and for the fluorine and chlorine contents of organic compounds containing fluorine alone, and fluorine and chlorine together, respectively, show satisfactory reproducibility and good agreement with the theoretical values. M. E. DALZIEL

Determination of Hydrogen in Fluorine-containing Halohydrocarbons. J. F. Miller, H. Hunt, H. B. Hass, and E. T. McBee (*Anal. Chem.*, 1947, **19**, 146–147)—Hydrogen in halo-hydrocarbons has hitherto been determined accurately only in absence of fluorine. The method described depends on the liberation of hydrofluoric and hydrochloric acids, and titration with standard alkali, a correction for acidity due to the liberation of free chlorine being applied.



Apparatus—Nitrogen from *A* (see Fig.) is used to purge the apparatus, passing first through alkaline pyrogallol, *C*, a sulphuric acid scrubber, *D*, over copper gauze, *F*, heated in the combustion tube, *E*, to 600° C. by the furnace, *G*, and dried finally by passing through the calcium chloride drying tube, *H*. The platinum combustion tube, *K* (32 in. by 0·5 in.), contains a 1-in. coil of platinum gauze, *M*, and is supported in a furnace, *T*, by a high-temperature combustion tube, *L*, the inlet of which is equipped with a ground platinum joint, *I*. The furnace has a thermocouple, *N*, a pyrometer, *O*, a tap transformer, *S*, and a safety switch, *R*. The absorption train consists of *P*, a 500-ml. Erlenmeyer flask with a Pyrex delivery tube made by sealing pieces of tubing 8 and 16 mm. in diameter together, and *Q*, a 250-ml. flask with an 8-mm. diameter delivery tube dipping below the surface of the water in it.

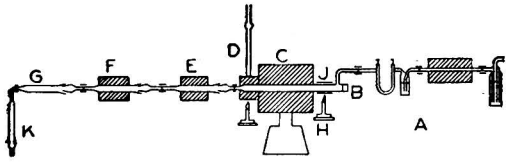
Procedure—Weigh a 0·20- to 0·35-g. sample, using a Pyrex vial, such as *J*, if the sample is a liquid boiling below 200° C., or a platinum boat if the material is less volatile. Place gauze wicks dipping into water round each end of the combustion tube about 1 in. from the furnace, and adjust the tube so that about 6 in. project from the inlet end of the furnace. Heat to 1300° C., and purge with nitrogen for 5 min. Connect *P*, containing 150 ml. of re-distilled water, 250 ml. of which should require less than 0·30 ml. of 0·1 *N* alkali to neutralise it to phenolphthalein, by means of rubber tubing, and adjust the nitrogen flow to 30 to 40 bubbles per min. through the delivery tube. If the ratio of hydrogen to halogen is greater than 1 : 1, add chlorine with the nitrogen, passing it first over phosphorus pentoxide. Open the inlet of the tube, and push the sample-container to a point about 2 in. from the open end. Close the tube quickly and attach the rest of the absorption train. When carbonaceous material stops coming out of the tube, remove the cooling wick from the inlet end, and push the tube into the furnace a further 1 cm. every 5 min. If a glass vial is used, avoid pushing it into the furnace zone, lest it be sealed before volatilisation is complete, or melt and stick to the platinum. If a platinum vessel is used, push the tube as far as possible into the furnace without damaging the rubber connections. For more volatile samples, 30 min. are sufficient for decomposition, but 45 min. are necessary for the higher-boiling samples. Sweep the combustion products out by passing nitrogen for a further 15 min., then draw the tube back to burn any condensed material, and remove first *Q* and then *P* at the combustion tube. The smaller vessel, *Q*, collects the excess of free chlorine or other volatile combustion products.

Filter the solution in *P*, and if fluorine is the only halogen present, boil for 5 min. and titrate hot with standard 0·1 *N* alkali to the phenolphthalein end-point. If chlorine was present in the sample, with or without fluorine, dilute the filtrate to 500 ml. and treat a 100-ml. aliquot portion with 1 ml. of 30 per cent. hydrogen peroxide solution. Boil for 5 min. and titrate hot with standard alkali as above. Treat another 100-ml. aliquot portion in an iodine flask with 10 ml. of 6 *N* sulphuric acid and 10 ml. of 30 per cent. potassium iodide solution. Shake, and allow to stand, after stoppering, for 10 to 15 min. Titrate immediately with standard 0·1 *N* thiosulphate in the presence of starch. Determine and apply a blank correction for the distilled water and reagents used. The percentage of hydrogen in the sample

$$\frac{100 \times 500 \times 0{\cdot}001\ (\text{ml. of } N\ \text{NaOH} - \text{ml. of } N\ \text{Na}_2\text{S}_2\text{O}_3)}{\text{wt. of sample in g.} \times \text{vol. of aliquot in ml.}}$$

Results—On five compounds, containing less than 2 per cent. of hydrogen, the maximum deviation of the mean from the expected value was approximately 1 in 35 on hydrogen contents; the method should be applicable also to higher contents. Errors are incurred by (i) incomplete decomposition when the sample is volatilised too rapidly, (ii) inaccurate and infrequent blank determinations, (iii) traces of oxygen remaining in the nitrogen, and (iv) the possible loss of fluorine by etching of the Pyrex receiver. This last source of error can be eliminated by using a platinum delivery tube in *P*. The combustion tube should be cleaned before each determination by passing air through it with each part of the tube in the furnace zone in turn. M. E. DALZIEL

Simultaneous Determination of Carbon, Fluorine, and Chlorine in Halocarbons. Semi-micro method. R. O'D. Teston and F. E. McKenna (*Anal. Chem.*, 1947, **19**, 193–196)—Absorption of silicon tetrafluoride by alumina is quantitative, and the use of elevated temperatures prevents carbon dioxide absorption, a simple absorption tube being applicable. A silver-packed tube is used to absorb chlorine and bromine.



Method—Pass oxygen, purified as usual for combustion methods, into a 69-cm. quartz combustion tube, B, of 7-mm. internal diameter and 11-mm. external diameter. The side-arm is 2 mm. in internal diameter, and 6 mm. in external diameter, and is attached 4 mm. from the end of the main tube. The capillary tip is 3·5 cm. long, and of 2-mm. internal and 3·5-mm. external diameters. The packing of the tube consists of six, 3·5-cm., platinum gauze rolls alternated with crushed quartz, so spaced that a platinum roll is at the entrance of the 1000° C. furnace, C, and at the junction of C and D. D is a 7-cm. furnace maintained at 175° C. by boiling *p*-cymene in order to protect the rubber connections from the higher temperature furnace; use of special joints to obviate this effect would be advantageous. E is a 21-cm. furnace at 295° C., and heats the 31-cm. long, soft-glass absorption tube, tightly packed with 2- to 4-mm. lengths of silver wire. F is a 17-cm. furnace at 175° C., and heats another soft-glass absorption tube containing alumina, sodium fluoride, and Drierite. The alumina zone is heated in the furnace, and the sodium fluoride serves to separate the Drierite from the hot region. G is a 20-cm. absorption tube containing Ascarite to remove carbon dioxide. K, containing Ascarite and Drierite, is a safety tube at the end of the train. All joints are glass-to-glass, held in place by heavy-walled, paraffin-impregnated, rubber capillary tubing.

Procedure—Weigh a 20- to 30-mg. sample into a Pyrex capillary tube if the sample is a liquid or a low-melting solid, and into a platinum micro-combustion boat, if a high-melting solid. Connect the train, and heat for 10 min. to allow the absorption tubes to reach the necessary temperature. Cool the centre of the combustion tube with a moist chamois leather before introducing the sample. Scratch the tip of the capillary, insert the capillary into the cool zone, and break it with a micro-spatula. Stopper the tube immediately. Remove the chamois leather, and apply a small micro-burner flame, H, 3 in. below and 1 in. behind the sample to volatilise it; increase the flame gradually until the sample is driven from the container. Set J, a 7-cm. roll of iron gauze, over the capillary and heat with the full micro-burner flame until vaporisation is complete, then pass oxygen in at 10 ml. per min. for 20 min. Remove, wipe, and cool the absorption tubes for 20 min., and weigh them.

Bromine and chlorine are absorbed together. If the sample contains hydrogen, water is absorbed in the Drierite of the alumina tube, thus vitiating results, unless the hydrogen is separately determined. Errors are also incurred in the halogen figures, as hydrogen fluoride attacks the silver absorption tube. Carbon is determined by calculation from the carbon dioxide absorbed.

Results—The method was developed as samples were analysed, the earlier decompositions taking place at 925° C. Higher results were obtained at 1000° C., and it seems that a temperature of 1100° C. might be preferable. Thus, the results tabulated in the original paper are not truly representative of the efficiency of the method as described, which is estimated to be ±0·3 per cent. on the carbon content, ±0·4 per cent. on fluorine, and ±0·9 per cent. on other halogens.

The temperature of the alumina required for quantitative absorption seems to be dependent on the surface conditions, as authors differ in their reports. The mechanism of absorption may be represented by the equations $2H_2O + SiF_4 = SiO_2 + 4HF$, and $6HF + Al_2O_3 = 2AlF_3 + 3H_2O$. This is borne out by the greater rate at which the Drierite is consumed in the alumina tube. Alumina is dried for 4 hr. at 175° to 180° C. before packing, and requires renewal after about 20 to 25 determinations, whilst the Drierite must be removed after 4 determinations. The silver packing also lasts for only 4 determinations; increased surface would be advantageous, but the oxygen-flow must not be obstructed. M. E. DALZIEL

Inorganic

Polarographic Determination of Sodium or Potassium in Various Materials. J. R. Weaver and L. Lykken (*Anal. Chem.*, 1947, **19**, 372–376)—The polarographic wave produced by sodium or potassium ions in a solution containing tetra-ethylammonium hydroxide as supporting electrolyte is suitable for the determination of either of these metals in a variety of materials. The tetra-ethylammonium hydroxide solution is prepared by adding 12 g. of silver oxide to a solution of 21 g. of tetra-ethylammonium bromide in 100 ml. of water, stirring for 15 min., and decanting the supernatant liquid. This solution should give a polarographic step less than 10 mm. in height at −1·95 v. *versus* the mercury anode. If the solution is unsatisfactory, the bromide and silver oxide must be further purified.

The procedures described are equally applicable to the determination of sodium or potassium, but not of mixtures of the two unless the relative amounts of sodium and potassium are known.

PROCEDURE—*Aqueous solutions of sodium salts*—This procedure is applicable to solutions containing no interfering substances. The same procedure is used to prepare a calibration curve for subsequent determinations. Add 1 ml. of the solution, or of a suitable dilution, to 5 ml. of tetra-ethylammonium hydroxide solution in a polarographic cell, pass

nitrogen through the solution to remove dissolved oxygen, and record a polarogram over the range of potential from −1·5 to −2·3 v. *versus* the mercury anode.

In the following procedures, the preparation of a solution containing the sodium ions free from interfering substances is described. The determination of the sodium in this solution is then carried out in exactly the same way as in the above case.

Aluminium oxide—To avoid the difficult separation of small amounts of sodium from aluminium, advantage is taken of the fact that strong alkalis react with aluminium ions to form aluminate ions which do not interfere with the determination. Weigh 500 mg. of the finely ground sample into a 500-ml. conical flask, and dissolve in 10 ml. of 18 *N* sulphuric acid by heating gently. Evaporate the acid by passing air from a glass jet through the flask, which is uniformly heated, until no more acid fumes are visible and the flask walls are completely dry. Cool, add 25 to 30 ml. of water, boil until solution is complete, transfer quantitatively to a 25 ml. volumetric flask, and dilute to 25 ml.

Silica—Weigh 500 mg. of the finely ground material into a platinum dish, moisten with a little water, add 5 ml. of hydrofluoric acid, and evaporate to complete dryness on a hot-plate. Repeat this twice more, and then add 10 to 15 ml. of water. Heat near boiling for several minutes, transfer to a 25-ml. volumetric flask, and dilute to 25 ml.

Combined aluminium and silica—In order to avoid dissolving sodium from the apparatus, special glass or silica ware should be used. To 500 mg. of the finely ground sample moistened with water in a platinum dish, add three 5-ml. portions of 48 per cent. hydrofluoric acid. Evaporate to dryness after each addition, then add 10 ml. of 18 *N* sulphuric acid, and evaporate until fumes appear. Add 10 to 15 ml. of water and transfer to a 250-ml. flask. Evaporate to dryness, removing the sulphuric acid fumes by means of a jet of air from a silica tube, dissolve the residue in hot water, transfer quantitatively to a 25-ml. flask, and dilute to 25 ml.

Iron oxide—Advantage is taken of the solubility of ferric chloride in ether to remove iron which interferes with the analysis. Dissolve 500 mg. of the finely ground powder in a beaker covered with a watch-glass by heating gently with 9 ml. of concentrated hydrochloric acid and 7 ml. of water, without boiling the liquid. Transfer the cool solution to a 50-ml., stoppered, graduated cylinder, rinsing the beaker with about 8 ml. of the hydrochloric acid, add 25 ml. of diethyl ether, and shake vigorously for 20 sec. When the phases have separated, remove the ether layer. Repeat the extraction until the solution is colourless, transfer to a beaker, and evaporate to 1 ml. Add 1·0 *N* tetra-ethylammonium hydroxide dropwise until the solution is neutral to litmus, add 1 drop in excess, heat for a few minutes, cool, and dilute to 25 ml. in a volumetric flask.

Calcium salts—Large amounts of calcium interfere with the determination. They are reduced to a safe level by precipitation with ammonium carbonate as follows. Dissolve 500 mg. of the sample in sulphuric acid, evaporate the excess of acid until calcium salts begin to precipitate, dilute to 100 ml., and neutralise with aqueous ammonia, adding a few drops in excess. Add 10 ml. of a saturated solution of ammonium carbonate, scratching the beaker until a precipitate appears, allow to stand for several hours, and filter off the calcium carbonate. Wash the precipitate with dilute ammonium carbonate solution, evaporate the combined filtrate and washings to a small volume, and then evaporate the solution to dryness and ignite the residue at 650° C. in a platinum dish. Leach the residue with hot water, cool, transfer the solution quantitatively to a 25-ml. volumetric flask, and dilute to 25 ml.

Copper salts—Copper must be removed as follows. Dissolve 500 mg. of the sample in 2 ml. of sulphuric acid, dilute to 100 ml., heat to boiling, and pass a rapid stream of hydrogen sulphide through the solution until it is cool. Filter the precipitate and wash it with 0·5 *N* sulphuric acid saturated with hydrogen sulphide. Evaporate the combined filtrate and washings to complete dryness in a beaker, and when cool dilute to 25 ml. in a volumetric flask.

Organic material—Low concentrations of sodium in organic material can be determined by the use of a large sample. Weigh a known amount of the sample into a platinum dish, evaporate it over a hot-plate, and ignite it over a bunsen flame and finally in a muffle furnace at 550° C. until all organic material is destroyed. When cool, dissolve all the sodium salts in hot water, transfer the cooled solution quantitatively to a 25-ml. volumetric flask, and dilute to 25 ml.

The methods described are accurate to within ±3·0 per cent. J. G. WALLER

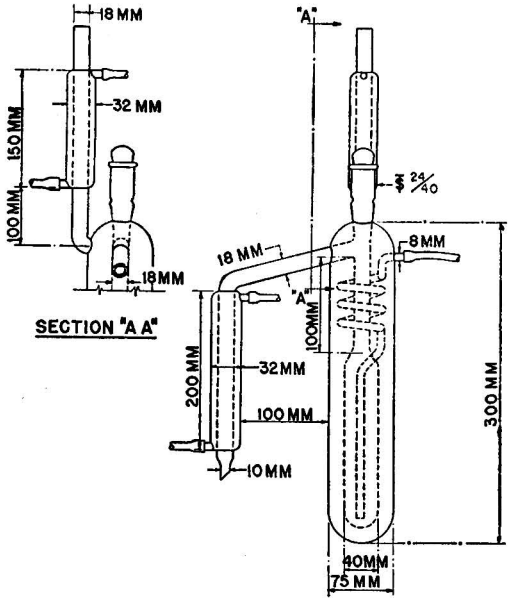
Constant-Temperature Steam-Distillation Apparatus for the Isolation of Fluorine. W. B. Huckabay, E. T. Welch, and A. V. Metler (*Anal. Chem.*, 1947, **19**, 154–156)—Constant temperature (145° C.) is attained by boiling tetrachloroethane under refluxing conditions in a jacket surrounding the distillation vessel. The disadvantages of earlier forms of the method are overcome by using the apparatus described.

Apparatus—This (see Fig.) is constructed in one piece from Pyrex glass. Add re-distilled *sym*-tetrachloroethane until the distillation bulb is three-quarters covered. The sample and sulphuric acid are introduced into the bulb, and steam is passed in, being pre-heated in the glass coil, through the 8-mm. inlet. The distillate emerges through the 18-mm. side-arm, is condensed in the water-condenser, and collected in a 100-ml. volumetric flask. The apparatus is heated by a 750-watt shallow-cone electric heater, and the steam generator by a 250-watt immersion heater.

Procedure—Add 20 ml. of 98 per cent. sulphuric acid to the bulb by means of a funnel extending well below the side-arm. Add up to 50 ml. of the sample, and remove the funnel, rinsing it with water. Place the glass plug in the ground-joint. Turn on the heater and pass a slow current of

steam to mix the solution. When the tetrachloroethane begins to reflux, increase the steam current until distillation occurs at a rate of 5 ml. per min. Continue until 100 ml. of distillate are collected, and turn off the heaters. When the apparatus has cooled to 50° C., another sample may be introduced.

When sulphate interferes in the fluoride determination, as in the thorium titration, determine a blank correction, after the operating conditions



are established, by distilling a second, 100-ml. portion. So long as these conditions are maintained, it is unnecessary to determine the correction more than once a month.

If the sulphuric acid contains fluoride, distil 20 ml. with 50 ml. of water and collect 100 ml. of distillate before adding the unknown fluorine compound.

Results—Sixteen results, all of which, except three, are within ±1 per cent. of the theoretical value, are given for the determination of 0·03 to 0·91 mg. of fluorine added as sodium fluoride, in the presence or absence of freshly precipitated silica, or barium sulphate, or dissolved alumina. This deviation represents the accuracy of the titration itself, so the distillation is probably better. Large amounts of chloride should be removed by precipitation with silver ions. The effect of boric acid was not tested, but has been reported to be similar to that of silicic acid, so probably does not interfere.

The apparatus permits temperature control to 0·5° C., and the tetrachloroethane charge lasts a year without deterioration. A distillation can be effected in 0·5 hr., and in the absence of high concentrations of salts in the samples analysed, the apparatus need not be cleaned after each distillation. Cleaning is effected by withdrawing the solution by means of a long-glass tube attached to a water-pump, rinsing with water, and passing a current of steam to clean the inner tube, withdrawing the liquid as before. M. E. DALZIEL

Determination of Chlorine Ion by Amperometric Titration. I. A. Korshunov and A. B. Gurevich (*Zavod. Lab.*, 1945, **11**, 648–651)—Determination of chloride may be carried out amperometrically with lead nitrate if alcohol be added to suppress the solubility of lead chloride and an easily-made correction be applied to the end-point to allow for unprecipitated lead chloride.

With increasing content of alcohol the solubility of lead chloride in water - alcohol mixtures decreases very rapidly at first and then tends to be approximately constant. In presence of sodium nitrate, at 25° C., 60 per cent. ethyl alcohol dissolves 3 mg.-mol. per litre, 60 per cent. dioxan dissolves 4 mg.-mol. per litre, and 60 per cent. methyl alcohol dissolves 9·8 mg.-mol. per litre. If amperometric titrations are carried out in solutions containing sufficient ethyl alcohol to give a concentration of 55 to 60 per cent. of alcohol at the equivalence point, the concentration of dissolved lead chloride is the same in all titrations, and corresponds to a definite wave-height under the conditions used. Thus, a correction may be made, and the true equivalence point found, by finding the intersection of the rising portion of the curve with a line, parallel to the volume (of titrant) axis, but at a distance from the horizontal part of the titration curve equal to the wave-height of the lead in solution.

Procedure—To 2 to 4 ml. of the solution containing chloride, add 3 to 6 ml. of ethyl alcohol to give a 55 to 60 per cent. concentration at the equivalence point and titrate amperometrically at 0·9 to 1·1 v., using a dropping mercury electrode, with standard lead nitrate of a concentration equivalent to two or three times that of the chloride. Draw the titration curve, and correct for lead chloride in solution, as indicated above. G. S. SMITH

Physico-chemical Analysis of Systems Important in Analytical Chemistry. The System AlF_3 - NaF - H_2O. [Gravimetric Determination of Aluminium as $11NaF.4AlF_3$.] I. V. Tananaev and J. L. Lelchuk (*J. Anal. Chem. Russ.*, 1947, **2**, 93–102)—Physico-chemical analysis of the system AlF_3 - NaF - H_2O indicates the existence of two salts, corresponding to the compositions $11NaF.4AlF_3$ and $3NaF.AlF_3$. The former is identical with natural cryolite from Greenland, and hence the usually accepted formula for cryolite is incorrect. The $11NaF.4AlF_3$ is congruently soluble and exists until the concentration of sodium fluoride in solution attains 1·4 per cent.; after this, the latter salt, which is incongruently soluble, is stable. For analytical purposes, $3NaF.AlF_3$ would not be suitable since it would be necessary to use for washing a sodium fluoride solution of at least 1·5 per cent. On the other hand, $11NaF.4AlF_3$ is suitable if its solubility is depressed by addition of alcohol.

The solubilities of the salt $11NaF.4AlF_3$, in g. per

100 ml. of various alcohol - water mixtures at 25° C., are: 0 per cent. alcohol, 0·0509; 24 per cent. alcohol, 0·0405; 48 per cent. alcohol, 0·0216; 64 per cent. alcohol, 0·0096; 76 per cent. alcohol, 0·0086; 96 per cent. alcohol, 0·0065.

Determination of aluminium—To 40 ml. of an aluminium chloride solution containing 0·02 to 0·08 g. of aluminium, add an excess of 3·3 per cent. sodium fluoride solution (about 30 ml.), and centrifuge after 5 to 10 min. Wash, by centrifuging, with 0·5 per cent. sodium fluoride solution two or three times, and then wash twice with 50 per cent. alcohol saturated with the salt. Dry at 125° to 130° C., and weigh. Results are accurate to within 1 or 2 mg. G. S. SMITH

Physico-Chemical Analysis of Systems Important in Analytical Chemistry. VII. Determination of Lead in the Form $K_2SO_4.PbSO_4$. I. V. Tananaev and I. B. Mizetzkaja (*Zavod. Lab.*, 1946, **12**, 529–533)—The double salt $K_2SO_4.PbSO_4$ occurs when the excess of potassium sulphate in solution is not less than 0·0234 g.-mol. per litre. This figure is in good agreement with 0·0225 g.-mol. per litre, found by Randall and Shaw (*J. Amer. Chem. Soc.*, 1935, **57**, 427). The use of this salt for the gravimetric determination of lead is preferable to that of the simple sulphate; its solubility is insignificant, mineral acids, including nitric acid, need not be removed by evaporation with sulphuric acid (the excess of potassium sulphate present withdraws hydrogen ions), and the double salt has a higher molecular weight (factor for conversion to lead, 0·4340).

Procedure—Add the solution containing lead to a potassium sulphate solution in amount sufficient to provide an excess of at least 25 ml. of 0·2 *M* potassium sulphate (a larger excess has no harmful effect). Make up the volume to 100 to 125 ml. and shake vigorously. The precipitate settles completely in 2 or 3 hr., but the solution may be filtered after 15 to 20 min. without difficulty or loss. Filter through a dried and weighed filtering crucible, wash with 0·025 to 0·03 *M* potassium sulphate (and finally with alcohol if the lead content is small and the potassium sulphate left by the wash liquor cannot be ignored), dry, and weigh. The crucible may be subsequently cleaned by successive treatments with thiosulphate, hot water, nitric acid, and water.

Variations in the method of precipitation have no effect. Thus, equally good results are obtained by adding lead nitrate solution dropwise, with constant stirring, to potassium sulphate solution, and by adding potassium sulphate solution rapidly to lead nitrate solution. With 0·5 g. of copper sulphate, 0·5 ml. of concentrated nitric acid, and 30 ml. of 0·2 *M* potassium sulphate, added to 120 ml. of lead nitrate solution, containing 0·0900 g. of lead, the amount of lead found was 0·0901 to 0·0906 g., indicating satisfactory precipitation in the presence of large amounts of copper in nitric acid solution. The method should, therefore, find application in the analysis of alloys.

G. S. SMITH

Potentiometric Determination of Beryllium. V. M. Tarayan (*Zavod. Lab.*, 1946, **12**, 543–546)—Beryllium may be titrated with sodium fluoride by the potentiometric method used by Treadwell and Bernasconi (*Helv. Chim. Acta.*, 1925, **8**, 500) for determining aluminium. Beryllium, like aluminium, forms complexes of the type $MBeF_3$ and M_2BeF_4, where M is a univalent metal, which, however, unlike the aluminium complexes, are easily soluble in water. With beryllium, hydroxyl ions are formed during the titration; apparently, beryllium is in the form of a basic salt which loses its hydroxyl as the complex fluoride forms. This prevents a sudden change of potential at the equivalence point unless the initial *p*H is about 2·5. Magnesium has no effect on the titration, but aluminium seriously interferes.

Procedure—Mix 10 to 20 ml. of the solution containing the equivalent of 0·005 to 0·1 g. of beryllium oxide, with an equal volume of alcohol, and add 0·2 *N* hydrochloric acid until the solution becomes just orange to methyl orange. This corresponds to *p*H 2·5 (approx.) in 50 per cent. alcohol. Saturate the solution with sodium chloride and pass carbon dioxide gas for 10 min. to remove air. Add 1 ml. of ferrous ammonium sulphate solution, saturated in the cold, and titrate, during the passage of carbon dioxide gas, with 0·5 to 0·6 *N* sodium fluoride, using a smooth platinum indicator electrode, and a saturated calomel standard electrode. Results are accurate to about 1 in 200. The potential drop is observed only after quantitative formation of Na_2BeF_4. G. S. SMITH

Colorimetric Determination of Small Quantities of Aluminium in Beryllium Salts. R. V. Mervel (*J. Anal. Chem. Russ.*, 1947, **2**, 103–110)—A method suitable for the determination of 0·002 to 0·5 mg. of aluminium in presence of 0·1 g. of beryllium sulphate (*e.g.*, in the analysis of beryllium oxide used for luminophors) is described. It depends upon a determination of the colour intensity of a benzene extract of the aluminium 8-hydroxyquinoline complex.

Extraction and colorimetric determination of aluminium—Extraction of aluminium oxinate from slightly acidic aqueous solutions, containing an excess of 8-hydroxyquinoline, by amyl alcohol or ethyl ether, is considered unsatisfactory. With amyl alcohol, the colour intensity of the alcoholic layer is insensitive to changes in the aluminium content, and both the alcoholic and aqueous layers are cloudy [*cf.* Kuskova, *Ibid.*, 1947, **2**, 7, who claims that *iso*amyl alcohol is suitable—Abstractor]. Benzene, however, gives satisfactory results; the intensity of the bright yellowish-green colour of the extract is directly proportional to the aluminium content, and the aqueous layer becomes colourless. In absence of aluminium, both layers are colourless. The optimum conditions for determining aluminium in 20 to 25 ml. of solution are given by acidifying the solution with 1 drop of *N* HCl (to give a *p*H of 3·5 to 3·6), adding 0·5 ml. of 5 per cent. oxine solution in 2 *N* acetic acid, followed by 3 ml. of 2 *N* ammonium acetate (added

in two stages: 1 ml. at first, and then 2 ml. after mixing), and then shaking with 10 ml. of A.R. benzene to give an extract for comparison with standards. Under these conditions, the minimum amount of aluminium that can be detected is 0·002 mg., and the upper limit for matching purposes is 0·5 mg.

Effect of beryllium—In presence of 100 mg. of beryllium sulphate the intensity is practically the same as in its absence if the aluminium content is 0·1 mg. or less, but above this the intensity is somewhat lower.

Effect of other elements—Removal of iron is essential. By a single treatment with sodium hydroxide and washing of the insoluble matter with hot water, the loss of aluminium by adsorption on the ferric hydroxide does not exceed 0·0005 mg. when 0·005 mg. of aluminium, 0·01 mg. of iron, and 100 mg. of beryllium sulphate are originally present. Zinc or cadmium in amounts up to 0·5 mg. has no effect. Titanium, nickel, and certain other metals do not interfere since they are precipitated by alkali.

Procedure—To 5 ml. of the solution containing 0·1 g. of beryllium sulphate, add 5 per cent. sodium hydroxide solution dropwise, with stirring, until the reaction is alkaline to litmus and then add 10 drops in excess. Heat at 100° C. for 15 min., filter into a 35-ml. tube fitted with a ground-glass stopper, and wash the insoluble matter twice with 5 ml. of hot water. Neutralise the filtrate to litmus with *N* hydrochloric acid, and add 1 drop of acid in excess. Proceed as described above. Compare with standards prepared in exactly the same way. [*Cf.* Gentry and Sherrington, ANALYST, 1946, **71**, 432, who used chloroform for extraction of aluminium oxinate.—Abstractor.] G. S. SMITH

Analysis of Zinc Cyanide Electrolyte Containing Sodium Sulphite. A. M. Guiva (*Zavod. Lab.*, 1945, **11**, 617)—*Determination of cyanide*—Dilute 25 ml. of the electrolyte with water to 500 ml. in a graduated flask, place 25 ml. of the diluted solution in a beaker, add 25 ml. of saturated bismuth nitrate solution, filter off the precipitated bismuth sulphite and hydroxide, washing 8 to 10 times with cold water, and collect the filtrate in a 250- to 300-ml. flask. To the filtrate add 10 ml. of 10 per cent. potassium iodide solution, and titrate with 0·1 *N* silver nitrate, preferably in a dark room under standardised lighting conditions.

Determination of total alkalinity—Place 25 ml. of the diluted electrolyte (see above) in a 300- to 500-ml., flat-bottomed flask, add 5 to 10 ml. of approximately 0·1 *N* iodine to oxidise the sulphite, then 25 ml. of potassium ferrocyanide solution (22 g. in 1 litre) to precipitate zinc, and finally 25 ml. of 1 per cent. silver nitrate solution to precipitate cyanide. Titrate the alkali with 0·2 *N* hydrochloric acid in presence of 2 or 3 drops of 1 per cent. phenolphthalein solution until the pink colour disappears, then leave for 1 or 2 min., and titrate to the end-point with the same acid.

G. S. SMITH

Polarographic Determination of Zinc in Metallic Cadmium after Preliminary Separation of Cadmium by Electrolysis on an Aluminium Cathode. P. N. Kovalenko and V. L. Dmitrieva (*J. Anal. Chem. Russ.*, 1947, **2**, 85–92)—The use of aluminium electrodes for electrolytic removal of cadmium prior to the determination of zinc is recommended. They are superior to platinum on the grounds of cheapness and availability, and they require no preliminary treatment. The dissolution of aluminium from the anode does not interfere with the subsequent polarographic determination of zinc (and other metals), and the precipitation of aluminium hydroxide that may take place during the electrolysis has little effect on the results, even if the aluminium hydroxide is not removed. It is better, however, to avoid this precipitation by using a buffered citrate medium (0·045 to 0·13 *M* potassium citrate) at *p*H 4·0 to 4·5. Under these conditions, and at 100° C., cadmium can be completely or partially deposited (98 per cent. in 1 hr.) free from zinc if the voltage is kept between 0·90 and 1·1 v. Polarographic determination can then be made after addition of aqueous ammonia solution, until alkaline to phenolphthalein, and of ammonium chloride; without these additions, the zinc wave is poorly defined.

The separation of cadmium and the determination of zinc take only 2 to 2·5 hr. in all, and the results, on synthetic mixtures, are accurate to 2 or 3 parts per 100, with 3 mg. of zinc in presence of 0·3 g. of cadmium. The method is applied to the determination of amounts of the order of 0·1 per cent. of zinc in metallic cadmium.

Procedure—Dissolve 0·5 to 0·6 g. of cadmium metal in a mixture of hydrochloric and nitric acids, evaporate to remove oxides of nitrogen, add sulphuric acid, and evaporate to sulphur trioxide fuming. Add water and evaporate nearly to dryness; dissolve the residue in water, add 2·0 to 6·0 g. of potassium citrate and 0·3 g. of dextrin, and then add sulphuric acid until the *p*H is 4·0 to 4·5 (methyl orange). Dilute the solution to about 150 ml., and electrolyse at the boiling point, with aluminium electrodes, at 0·90 to 1·1 v. for 1 hr. Wash the electrodes with water and transfer the electrolyte to a 200-ml. graduated flask. Cool, add 40 ml. of 25 per cent. aqueous ammonia solution and 5 to 10 g. of ammonium chloride, together with 1 per cent. glue solution and sodium sulphite, make up to the mark, and obtain the polarogram for zinc. G. S. SMITH

Photo-colorimetric Determination of Chromium in Steel. I. V. Tananaev and K. A. Matveeva (*Zavod. Lab.*, 1945, **11**, 615)—The method is based on the oxidation of aniline hydrochloride by chromic acid. The colour intensity of the bluish-green solution is proportional to the chromium content.

Procedure—Dissolve 0·2 g. of steel in a 100-ml. graduated flask by heating with 25 ml. of a 1 + 1 mixture of diluted sulphuric acid (1 + 9) and diluted phosphoric acid (1 + 1). Add concentrated nitric acid in drops until frothing ceases, then boil to

remove oxides of nitrogen, add 25 to 40 ml. of 15 per cent. ammonium persulphate solution, and heat until a reddish coloration appears. Destroy manganic acid by heating with 2 or 3 ml. of 15 per cent. sodium chloride solution until the solution is pure yellow in colour and chlorine is removed. Cool the solution under the tap, make up to the mark, mix, and pipette 10 ml. into a 50-ml. graduated flask. Add 1 ml. of aniline hydrochloride solution, prepared by adding 30 ml. of pure aniline in small portions, with constant stirring, to 100 ml. of diluted hydrochloric acid (1 + 1). The solution should be kept in a glass-stoppered flask in the dark. Mix, and leave for 10 min. for the colour to develop (it is stable for 20 min.); then make up to the mark, transfer a portion of the solution to a 10-mm. cell, and measure the absorption in a photometer, allowing for a blank similarly prepared from a chromium-free steel. Determine the chromium content from a calibration curve based on measurements obtained with solutions of standard samples containing 0·2 to 1·6 per cent. of chromium.

The method is accurate to about 1 part in 20 at 0·2 per cent. of chromium and to 1 part in 50 at 1·5 per cent. of chromium. G. S. SMITH

Use of Diphenylthiocarbazone (Dithizone) in Analysis. II. Instability Constants of Zinc, Cadmium, and Lead Dithizonates. A. K. Babko and A. T. Pilipenko (*J. Anal. Chem. Russ.*, 1947, **2**, 33–42)—*Separation of zinc and cadmium* (final section of the paper)—From theoretical considerations, it is shown that zinc and cadmium cannot be separated by the dithizone method by choice of the *p*H, but cadmium dithizonate should interact with hydrogen sulphide and zinc dithizonate should not. Tests show that the orange-red solution of cadmium dithizonate in carbon tetrachloride immediately turns green, the colour of free dithizone, when the solution is shaken with hydrogen sulphide solution, whereas the colour of the corresponding zinc solution is unaffected. Freshly precipitated zinc sulphide added to a green dithizone solution gives a red colour due to the formation of the dithizonate, whereas cadmium sulphide does not react. The effect is obtained in the presence of buffers over the *p*H range 3 to 7, and thus the result does not depend upon *p*H. On the other hand, a mixed cadmium and zinc sulphide precipitate gives no reaction with dithizone solution, possibly because of the existence of solid solutions. The separation is satisfactory if the two metals are first converted to dithizonates and then treated with hydrogen sulphide. G. S. SMITH

Colorimetric [Absorptiometric] Determination of Red Lead (Minium). M. H. Swann (*Anal. Chem.*, 1947, **19**, 191)—The method is applicable both to unmixed red lead and to mixed pigments containing red lead. The oxide is dissolved in glacial acetic acid and the solution is diluted so that a clear yellow to red suspension of lead dioxide is produced.

$$Pb_3O_4 + 4CH_3COOH \rightarrow Pb(CH_3COO)_4 + 2PbO + 2H_2O$$

$$Pb(CH_3COO)_4 + 2H_2O \rightarrow PbO_2 + 4CH_3COOH$$

Procedure for use with unmixed red lead—Dry the sample *in vacuo* at 125° C. for several hours and weigh 0·5 g. into a dried 125-ml., glass-stoppered flask. Add exactly 20 ml. of fresh glacial acetic acid from a burette, stopper the flask immediately and shake for a few minutes to break up any lumps. Insert a small strip of paper at one side of the stopper and heat the flask in a water-bath at 60° C., shaking every few minutes until solution is complete. If necessary, stopper tightly and shake vigorously. When cool, the solution should be clear; any cloudiness or dark colour indicates that the materials or apparatus have not been free from water. Take an aliquot portion (0·25 ml. to 3·0 ml.) in a 600-ml. beaker and add immediately 5 ml. of absolute alcohol for each 0·25 ml. of solution and swirl for 2 or 3 sec. Add 225 ml. of cold distilled water, stirring rapidly. A colour develops at once. If a colour appears on adding the alcohol, either the acetic acid or alcohol contains water and the results will be incorrect. Measure the absorption immediately, using a Fisher electrophotometer with a green filter. Prepare a calibration curve by treating 0·5 g. of pure red lead as above, and taking a series of aliquot portions of the acetic acid solution.

Procedure for use with mixed pigments containing red lead—Extract the pigment from the wet paint by the usual centrifuge method, using anhydrous ether as the solvent. Dry the finely ground, sifted material (−100 mesh) as above. Weigh a sample containing at least 0·2 g. of red lead into a dry, 50-ml. centrifuge tube with a constricted neck. Add 20·0 ml. of glacial acetic acid, fit a rubber stopper to the tube and shake the tube for a few minutes. Place the tube in a water-bath at 60° C., loosen the stopper to release pressure, and shake the tube every few minutes. After 15 min., centrifuge and place exactly 1 ml. of the clear liquid in a 600-ml. beaker. Add quickly 20 ml. of absolute alcohol and swirl for 1 sec. Add 200 ml. of water, stirring quickly. Dilute the solution to 250 ml. in a graduated flask, and measure the absorption without delay.

Results are reproducible to about 0·1 mg. when the aliquot portion contains 30 to 60 mg. of red lead. Litharge is dissolved by the acetic acid, but does not precipitate on dilution. Lead dioxide is not dissolved. In the analysis of extracted pigments, some loss of red lead may be expected as the oxide readily forms soaps with fatty acids in the vehicle. L. A. DAUNCEY

Polarographic Determination of Lead and Tin in Ores. S. Yu. Faynberg and E. M. Tal (*Zavod. Lab.*, 1945, **11**, 631–634)—Lead - tin ores, containing tin as cassiterite, when treated with diluted hydrochloric acid, yield a solution containing all the lead, and an insoluble residue containing all the tin. Lead may be determined polarographically in the solution after addition of calcium or sodium hypophosphite. Tin may be determined in the insoluble portion after fusion with sodium hydroxide, extraction with water, and addition of hydrochloric acid and hypophosphite. The solution for the polarographic determination

of tin contains this element entirely in the stannous state, arsenic having been separated as the metal; iron, being in the ferrous state, does not interfere. The method does not require the use of hydrogen sulphide.

Under these conditions, silica, which has been found by certain other workers to interfere with the polarographic determination of tin, has no effect.

Procedure—Moisten 0·2 g. of sample, placed in a 100-ml. conical flask covered with a clock-glass, with a few drops of water, add 15 ml. of diluted hydrochloric acid (1 + 1), and boil for 20 min., stirring meanwhile. Filter through a close filter, washing the insoluble matter three or four times by decantation using small amounts of diluted hydrochloric acid (1 + 1), and collecting the filtrate in a 50-ml. graduated flask. *Determination of lead*—Add to the filtrate 1 g. of calcium or sodium hypophosphite, and heat until the solution becomes colourless, showing complete reduction of iron. (In presence of arsenic, however, a brown colour develops.) Cool the solution, make it up to the mark with diluted hydrochloric acid (1 + 1), transfer a portion to a polarographic cell, pass hydrogen gas for 10 to 15 min., and obtain the polarogram. Determine the lead content by the addition method.

Determination of tin—Wash the insoluble matter on to the filter by means of hot water, and continue washing with hot water until the washings contain no chloride. Ash the filter and insoluble matter in an iron crucible, cool, add 2g. of sodium hydroxide and heat gently until it is molten (about 5 to 10 min.). Stir the melt a few times, let it cool somewhat, and carefully drop into the still liquid mass about 0·5 g. of clean metallic sodium. Heat again for 5 to 10 min. Place the crucible while still hot in a 100-ml. beaker covered with a clock-glass and containing 10 ml. of hot water. After dissolution of the melt, remove the crucible and wash the latter with the minimum amount of water. The total volume of the solution should not exceed 20 ml. Transfer the solution to a 50-ml. graduated flask, add in two or three portions, 15 ml. of concentrated hydrochloric acid, and 1 g. of calcium or sodium hypophosphite, and heat to decolorise the solution. Cool, make up to the mark with concentrated hydrochloric acid, transfer a portion to a polarographic cell, pass hydrogen gas for 10 to 15 min., and obtain the polarogram, using the addition method or a solution containing pure salts (tin, iron, etc.) to establish the tin content.

If tungsten is present, fuse the acid-insoluble residue with bisulphate, and extract the melt with saturated ammonium carbonate solution. The insoluble residue then contains the tin, free from tungsten. G. S. SMITH

Detection and Colorimetric Determination of Niobium and Tantalum. M. S. Platonov and N. F. Krivoshlikov (*Trans. All-Union Conf. on Anal. Chem.*, 1943, **2**, 359–370)—Conditions for the formation of yellow colours by the addition of pyrogallol to niobium, tantalum, and titanium solutions are described. The individual oxides (0·01 to 0·05 g.) were fused with potassium bisulphate at 450° to 700° C. for 20 to 30 min., and the melts extracted with 100 ml. of hot, saturated ammonium oxalate solution. In presence of sulphuric acid, the tantalum solution gives with pyrogallol a yellow coloration that is intensified by addition of more sulphuric acid. Niobium gives a yellow colour only in alkaline or neutral solution, and the addition of sulphuric acid destroys it. Titanium gives a yellow colour in both acid and alkaline solution; addition of hydrogen peroxide destroys the colour due to pyrogallol but yields the characteristic colour of pertitanic acid. Hydrogen peroxide destroys also the colour of tantalum - pyrogallol solutions.

The reaction is sensitive to about 0·05 to 0·07 mg. of tantalum pentoxide in 1 ml. of solution, and, in this respect, compares favourably with the tannin reaction (Schoeller, *Z. anal. Chem.*, 1934, **96**, 252) which, however, has been found by the authors not to be sufficiently reproducible for quantitative work.

With pyrogallol solutions, niobium gives, in presence of sodium sulphite, a yellow colour in alkaline solution but none in acid, whilst tantalum gives a yellow colour in acid solution but not in alkaline solution. Thus, colorimetric determination of niobium and tantalum may be carried out by one of three methods—(i) The test solution is treated with sodium sulphite until the reaction is faintly alkaline; niobium is then determined with pyrogallol, after which sulphuric acid is added, and tantalum is determined similarly. (ii) Tantalum is first determined in acid solution, then sulphite is added to make the solution alkaline, and niobium is determined. (iii) The total niobium and tantalum are determined gravimetrically, and one of the metals is then determined with pyrogallol.

Standard solutions—For colour standards, solutions of ammonium chromate (5 g. in 250 ml. of water) or slightly alkaline methyl orange may be used, but it is preferable to prepare solutions from niobium and tantalum pentoxides under the same conditions as apply to the test samples. For niobium, fuse 0·008313 g. of the pentoxide with seven to ten times its weight of potassium bisulphate, extract the melt with 70 to 80 ml. of saturated ammonium oxalate solution, dilute to 100 ml., and mix with an equal volume of sulphite - pyrogallol solution (10 g. of pyrogallol in 250 ml. of saturated sodium sulphite solution; this solution is stable for 10 days). The resulting solution retains its colour intensity unchanged for 2 months. For tantalum, proceed as with niobium, but extract the melt with saturated ammonium oxalate solution and 10 ml. of concentrated sulphuric acid per 100 ml.

Determination of niobium, tantalum, and titanium—Fuse the oxides with bisulphate, extract the melt with ammonium oxalate acidified with sulphuric acid, and dilute to a suitable concentration (*cf.* preparation of standards). Add sulphite and pyrogallol, and compare the colour intensity with that of the standard niobium solution by means of a Duboscq colorimeter. Correct for titanium, which gives the same type of colour as niobium, by determining this element colorimetrically on a separate portion of the solution, using hydrogen

peroxide; the colour intensity, with pyrogallol, due to 0·0025 g. of titanium dioxide, corresponds to that given by 0·00415 g. of niobium pentoxide. Determine tantalum either colorimetrically in acid medium, or by difference (weight of total oxides less weight of niobium and tantalum pentoxides).

If the amount of titanium greatly exceeds that of niobium or tantalum, carry out a complete or partial separation of titanium by one of the published procedures. G. S. SMITH

Determination of Niobium in Steel. B. S. Krasilshchikov and N. M. Popova (*Zavod. Lab.*, 1945, **11**, 512–515)—A method, based on hydrolysis in dilute hydrochloric acid solution in presence of sodium sulphite, is described. It is more rapid than, and yet as accurate as, the cupferron method (Cunningham, *Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 233), and the perchloric acid method (Silverman, *Ibid.*, 1938, **10**, 287), and requires only reagents that are generally available. It is applicable to steels not containing titanium. Tantalum is determined colorimetrically with pyrogallol (Platonov and Krivoshlikov, *Trans. All-Union Conf. on Anal. Chem.*, 1943, **2**, 359) and allowed for.

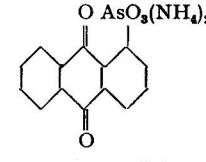
Experiments on the hydrolysis of niobium solutions with and without preliminary evaporation in presence of sulphuric acid were carried out. (i) Niobium pentoxide (0·0280 g.) was dissolved in hydrofluoric acid - sulphuric acid mixture and the solution evaporated twice with sulphuric acid to give a final volume of 2 ml.; 250 ml. of diluted hydrochloric acid were then added, the amount of acid being varied so that the final concentration was 2, 10 or 20 per cent. in terms of concentrated hydrochloric acid, and the solution was boiled for 5 min., after which it was kept for 30 min. at 80° to 90° C. The precipitate was filtered off, washed with hot 2 per cent. hydrochloric acid solution, ignited, and weighed as Nb_2O_5. Results showed that losses of 1 and 7 mg., respectively, occurred in the 10 and 20 per cent. acids, but that quantitative precipitation occurred in 2 per cent. hydrochloric acid. Addition of sodium sulphite had no effect. (ii) Niobium pentoxide (0·2 to 0·4 g.) was fused with potassium bisulphate, and the melt extracted with cold water. The insoluble niobic acid was filtered off, washed with water, and boiled with 100 ml. of concentrated hydrochloric acid for 5 min. Addition of water to yield a 1 + 2 hydrochloric acid concentration gave complete solution. The solution was diluted to 500 ml., and aliquot portions were diluted so that the final acid concentration was 2 per cent. by volume of concentrated hydrochloric acid. They were boiled for 3 to 5 min., and then kept at 60° to 80° C. Coagulation did not start in less than 20 to 30 min., the subsequent filtration was very slow, and the recovery of the pentoxide was incomplete (loss of 1 to 2 mg.). The introduction, however, of 2 g. of sodium sulphite before hydrolysis produced an immediate precipitate which coagulated well after 20 min., and yielded quantitative results.

Procedure—Dissolve 2 to 5 g. of steel in 25 to 50 ml. of diluted hydrochloric acid (1 + 1) and add a few drops of concentrated nitric acid to decompose chromium and iron carbides. Heat to remove oxides of nitrogen, dilute the solution to 300 ml. with hot water, add 2 g. of sodium sulphite, and boil for 5 min. Keep at 60° to 80° C. for 20 min., filter off the precipitate, wash it with warm, 2 per cent. hydrochloric acid solution, and ignite it in a platinum dish. Treat the residue with 3 ml. of concentrated sulphuric acid and remove silicon by evaporation in presence of hydrofluoric acid. Then evaporate twice with sulphuric acid to give a final volume of 1 or 2 ml. Wash the contents of the dish into a beaker by means of cold water, add 250 ml. of hot, 2 per cent. hydrochloric acid, followed by some paper pulp, and boil the solution for 5 min. Keep it at 60° to 80° C. for 20 min., filter, wash with warm, 2 per cent. hydrochloric acid, ignite the insoluble matter in a porcelain crucible, and weigh the mixed niobium and tantalum pentoxides. Fuse with potassium bisulphate, dissolve the melt in ammonium oxalate solution, and determine tantalum colorimetrically with pyrogallol. Calculate the niobium content by difference.

If the precipitate is contaminated with chromium fuse it with bisulphate, dissolve the melt in 5 per cent. ammonium tartrate solution, acidify with hydrochloric acid, and precipitate niobium with cupferron. If the steel contains molybdenum, determine the molybdenum content of the precipitate colorimetrically.

Results are accurate to ±0·02 per cent. (of the steel) over the range 0·15 to 1·40 per cent. of niobium. G. S. SMITH

Use of Anthraquinone-α-arsonic Acid for Determining Small Amounts of Tin. V. I. Kuznetsov (*Zavod. Lab.*, 1945, **11**, 263–266)—Small amounts of tin are difficult to separate from certain other elements by the ordinary methods, *e.g.*, nitric acid fails to give a precipitate with 0·1 mg. of tin in 100 ml. of solution, and in presence of large quantities of chlorides, hydrogen sulphide fails to precipitate tin sulphide. In special cases, *e.g.*, in sodium peroxide, 0·00001 per cent. of tin may be determined colorimetrically by means of anthraquinone-1-azo-4-dimethylaniline, "anthrazo", (Kuznetsov, *J. Appl. Chem. Russ.*, 1940, **13**, 769). The use of a new precipitating reagent, anthraquinone-α-arsonic acid, the ammonium salt of which,



has been named "anthraquas," is now described. It is suitable for precipitating tin in concentrations as low as 0·0005 mg. per litre. Larger amounts (more than 0·2 mg.) of tin may then be determined iodimetrically and smaller amounts (less than 0·2 mg.) by the anthrazo colorimetric method. Arsonic acids, in general, react strongly with β-compounds of quadrivalent tin and have little effect on α-compounds (Kuznetzov, *J. Appl. Chem. Russ.*, 1940, **13**, 1512). If the dissolution of tin

is effected by alkali treatment, then acidification with nitric acid and heating yields the β-compound, which, in presence of anthraquas, is immediately and quantitatively precipitated. Co-precipitation with tungstic acid, introduced as sodium tungstate, or precipitation by a large excess of the reagent (the free acid is soluble to the extent of only 0·04 per cent. at 20° C.), may be required with very small amounts of tin. With tin are precipitated similar compounds of zirconium, hafnium, niobium, tantalum, and titanium, and also elements which would be precipitated on acidification even in the absence of the reagent, but all these elements may either be separated by the process of "wet ignition," or be neglected, since with small amounts of tin they are present in quantities that do not interfere with the iodimetric or colorimetric determination of tin. Chlorides must be absent.

Method—It is assumed that tin has been brought into solution by an alkali process. For each 100 ml. of chloride-free solution add 10 to 20 ml. of a 1 per cent. aqueous solution of anthraquas and, if necessary, 1 ml. of 1 per cent. sodium tungstate solution. Then add chloride-free nitric acid (traces of chlorides may be rendered harmless by addition of silver nitrate) to neutralise the solution and to give an excess corresponding to about one-tenth the volume of solution, heat for 1 to 1·5 hours in boiling water, filter off the precipitate, and wash it with acidified, 3 per cent. ammonium nitrate solution. For "wet ignition" place the dried precipitate together with filter paper in a tall, 50-ml. porcelain crucible and add a mixture of 3 ml. of concentrated sulphuric acid and 1 ml. of concentrated nitric acid. Cover with a clock-glass (50 mm. diameter) that has been heated in the centre and pulled out by means of a pointed piece of iron to give a funnel. Heat on a sand-bath, and when the contents begin to blacken introduce through the funnel in the clock-glass a drop of concentrated nitric acid or some small crystals of ammonium nitrate, and repeat this procedure until the contents of the crucible no longer become black on further heating. Then heat more strongly until sulphuric acid fumes appear, and when the condensed vapours moisten the glass and the walls of the crucible, remove the clock-glass. To obtain an indication of the amount of tin present place a micro-drop on a glass slide by means of a 1-mm. diameter glass rod with a 2-mm. diameter spherical end, mix with two drops of 2 per cent. hydrochloric acid, saturated with sodium chloride, and test with anthrazo paper. A bright, dark bluish-violet spot indicates that there is sufficient tin present for an iodimetric determination; otherwise, the determination is made by means of anthrazo. In the latter case, evaporate the solution nearly to dryness, add 1 ml. of 2 per cent. hydrochloric acid saturated with sodium chloride, filter if necessary, and proceed as described previously (Kuznetov and Bender, *J. Appl. Chem. Russ.*, 1940, **13**, 1724). For the iodimetric determination, introduce into the crucible some small crystals of urea to destroy nitrosyl-sulphuric acid, if present, heat, then cool, and add 2 to 3 ml. of concentrated hydrochloric acid, and 2 to 3 ml. of 2 per cent. hydrochloric acid saturated with sodium chloride, filter off the insoluble material, and wash with a small quantity of 2 per cent. hydrochloric acid saturated with sodium chloride. Reduction and titration are carried out in a 50-ml. flask fitted with a Contat-Göckel valve. To the solution add 2 drops of a mixture of 10 per cent. solutions of cobalt and nickel chlorides, 5 drops of 20 per cent. potassium iodide solution, and 0·2 to 0·3 g. of aluminium drillings and, after dissolution of the aluminium, titrate as usual with 0·01 *N* iodine solution.

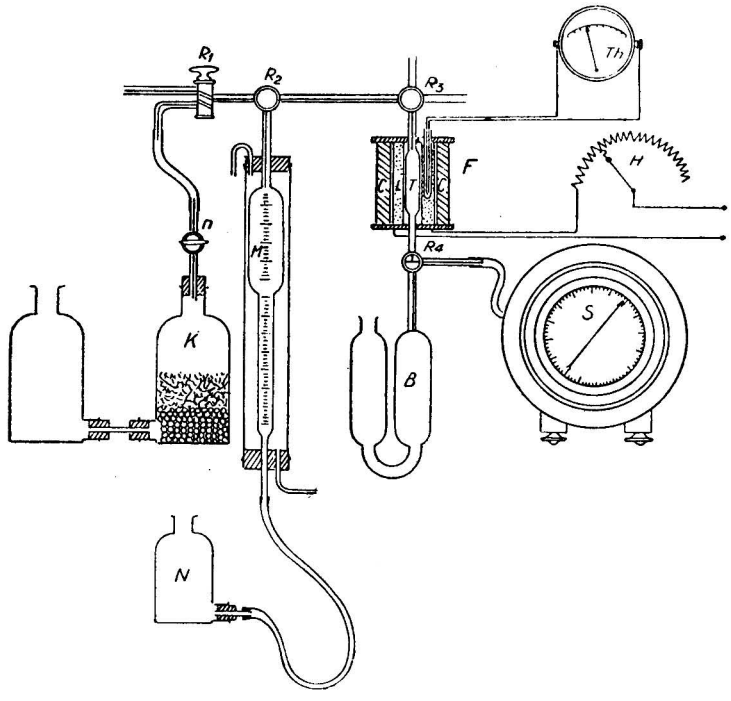
Preparation of anthraquinone-α-arsonic acid—A modification of Benda's method (*J. prakt. Chem.*, 1917, **95**, 82) is used. Gently heat 4 g. of sodium nitrite with 25 ml. of concentrated sulphuric acid to effect solution and mix it with a solution of 13·4 g. (0·06 g.-mol.) of α-aminoanthraquinone in 60 ml. of concentrated sulphuric acid. Test the mixture for the presence of sufficient nitrite by mixing 1 drop with water; no red precipitate of α-aminoanthraquinone should form. Pour the solution on to ice, filter off the precipitated diazonium compound, wash it with a small quantity of ice-cold water, and then suspend it in 200 ml of water. Prepare a solution of 8 g. of arsenious oxide, 5 g. of sodium hydroxide, and 5 g. of anhydrous sodium carbonate in 400 ml. of water, add to it a solution of 3 g. of copper sulphate in 30 ml. of water, and to this mixture, well cooled by addition of ice, add slowly underneath the surface of the liquid, with stirring, the suspension of the diazonium compound. Add ether to accelerate the removal of froth. Since it is necessary that the reaction mixture should remain alkaline to phenolphthalein all the time, add small portions of sodium carbonate when required. Allow the mixture to stand for several hours, then gently heat, and add an excess of concentrated hydrochloric acid and 15 ml. of sodium chloride for each 100 ml. of solution. Cool, filter the impure product, wash it with 5 per cent. hydrochloric acid, dissolve it by heating with sodium hydroxide solution, and re-precipitate with hydrochloric acid. For final purification, dissolve the washed precipitate in aqueous ammonia solution, filter, and precipitate with hydrochloric acid to give 11 g. of the free acid, yellowish in colour. To obtain a solution of the ammonium salt (anthraquas), dissolve the acid in aqueous ammonia solution, and boil off the excess of ammonia.

G. S. SMITH

Gas Analysis

Volumetric Determination of Traces of Oxygen in Nitrogen. M. Delassus (*Chimie Analyt.*, 1947, **29**, 151–153)—The method was developed to determine 0 to 0·15 per cent. by volume of oxygen in the nitrogen obtained by liquefaction of air for the synthesis of ammonia. The nitrogen is passed at 350° C. over a coppered silica gel, the resulting copper oxide reduced with a measured volume of pure hydrogen, and the loss of hydrogen measured. The coppered silica gel is prepared by soaking the gel in copper nitrate solution and then heating carefully to 300° C. In the

diagram, *M* is the measuring burette (100 ml. total, 20 ml. to bulb), *K* the Sainte-Claire Deville generator of pure hydrogen, *T* the tube of coppered silica gel, *F* an electric furnace, *L* a heat-balancing block of aluminium, *B* a reservoir, and *S* a gas meter or 5-litre aspirator.



Procedure—Purge the manifold thoroughly of air and pass 5 litres of the nitrogen in about 15 min. over the reduced copper, measuring the outgoing gas by the meter or aspirator. Pass 100 ml. of hydrogen from *M* three or four times to and from *B* and measure the change in volume. The loss of 1 ml. of hydrogen is equivalent to 0·01 per cent. of oxygen in 5000 ml. of nitrogen.

W. J. GOODERHAM

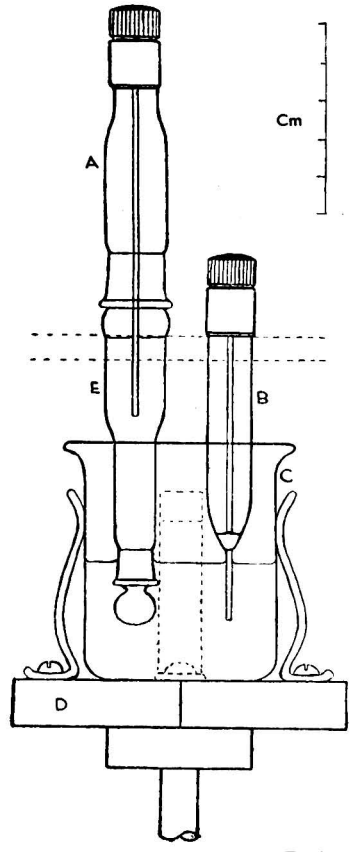
Determination of Fumigants. Part XVIII. Determination of Low Concentrations of Methyl Bromide. J. Russell (*J. Soc. Chem. Ind.*, 1947, **66**, 22–26)—Methyl bromide in samples of air collected during fumigation is oxidised by the catalytic combustion method of Lubatti and Harrison (*Ibid.*, 1944, **63**, 140), in which sodium bromide is formed. The bromide is determined by the method of Kolthoff and Yutzy (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 75), or by a potentiometric method, a necessary preliminary to the former method being the destruction of the peroxide introduced during the combustion.

Potentiometric method—The diagram shows the design of the electrode system. The two terminals are fixed to Pyrex tubes by a layer of picein wax and are soldered to silver wires. The tube of the indicator electrode B is drawn out so that the silver wire can be sealed into it by picein wax. The tube A of the reference electrode is joined to the lower tube, E, by a ground joint, and E is closed at the lower end by a ground stopper. The ground surface of the stopper is wetted sufficiently for there to be electrical contact between the solution and the contents of E. A suspension of silver bromide in 0·1 *N* potassium nitrate is contained in the lower part of the reference electrode. The solution is placed in a 100-ml. beaker fixed to a turn-table. For measuring the potential, a direct-coupled amplifier with negative feed-back was used. Details of the instrument are given.

Procedure—Transfer the alkaline bromide solution to the titration beaker, add neutral red solution, neutralise with 0·5 *N* sulphuric acid, and add 2 drops in excess. Titrate slowly with 0·001 *N* silver nitrate, added from a micro-burette, waiting after each addition until the potential is constant. Titrate until the needle of the milliameter is beyond the position obtained when the electrodes are immersed in distilled water containing a few drops of 0·5 *N* sulphuric acid. Determine the position of the end-point by a graphical method.

The concentrations of methyl bromide used varied between 0·1 and 40 mg. per litre, and samples analysed contained from 0·03 to 1 mg. of the methyl bromide. The order of the accuracy of the two methods was found to be about the same, the percentage standard deviations in figures for

the recovery of methyl bromide being, for the Kolthoff method, from 1 to 7 per cent., and for the potentiometric method, from 0·36 to 5 per cent.



B. ATKINSON

Microchemical

New Scheme for the Microchemical Analysis of Ferrous Alloys. E. J. Vaughan and C. Whalley (*J. Iron and Steel Inst.*, 1947, **155**, 535–562)—Methods are described for the determination of carbon, silicon, phosphorus, sulphur, manganese, nickel, molybdenum, chromium, vanadium, cobalt, copper, tungsten, titanium, and iron; they permit the determination of all these elements in approximately 80 mg. of most ferrous alloys. The methods are fitted into several composite schemes, one of which allows the determination of all the metals listed above in one 15-mg. sample. Simpler schemes covering a smaller number of metals are also given and may readily be adapted to any special circumstances or requirements. Most of the determinations are completed by absorption measurements on a Spekker instrument for which special cells have been designed to make efficient use of the beam of light with a small volume of liquid. Methods of preparing the samples and apparatus to facilitate the handling of the sample solutions are described. Carbon is determined gravimetrically by combustion of the sample in oxygen. The preferred details of the apparatus and technique are described. Sulphur is also determined by a combustion method which may be completed either by a titration or by an absorptiometric measurement. The original paper should be consulted for details of each method, and its scope, for several composite schemes, and for typical results and uses of the methods.

L. A. DAUNCEY

Physical Methods, Apparatus, etc.

Chromatographic Analysis of Rubber-Compounding Ingredients and their Identification in Vulcanisates. Parts I to V. L. J. Bellamy, J. H. Lawrie, and E. W. S. Press (**Parts I to III,** *Trans. Inst. Rubber Ind.*, 1947, **22**, 308–324; **Parts IV and V,** *Ibid.*, 1947, **23**, 15–25).

Parts I to III—The authors describe chromatographic procedures for identifying compounds used as accelerators of the vulcanising process, the separation of the material extractable from the vulcanisates by acetone into some of its characteristic components, and the identification among these of some of the accelerators or their reaction products.

Apparatus and materials—A vertical glass tube containing alumina (B.D.H. Activated Alumina for Chromatographic Adsorption) is connected to a receiving flask through an adaptor fitted with a side-arm. The side-arm is connected to a water-pump so that gentle suction can be applied. A slurry of alumina in benzene is formed and poured quickly into the column, which is plugged at the bottom with cotton wool. The alumina is allowed to settle under gravity, and a filter-paper disc is placed on top of it. Once the column is prepared, the top should not be allowed to become dry. The material is introduced in benzene solution and the chromatograph developed with benzene, alcohol - benzene (1 + 99), alcohol - benzene (5 + 95), and absolute alcohol, as necessary. When a sample of vulcanised rubber is being dealt with, the acetone extract is prepared (*e.g.*, as given by British Standard Methods of Testing Vulcanised Rubber, B.S. 903, 1940; or, Amer. Soc. Test. Mat. Standards on Rubber Products), dried, and redissolved in benzene.

Behaviour of components of vulcanisates other than anti-oxidants and accelerators—Paraffin wax and mineral oil are not adsorbed, and pass through on development with benzene. Fatty acid is strongly adsorbed and cannot be eluted with normal solvents. It can be separated from other components either by eluting the latter or by removing the fatty acid with alcoholic potash. Pine tar is strongly adsorbed at the top of the column as a brown-black band, and only one small yellow zone can be eluted from this with benzene. The rate of elution is very slow but is accelerated somewhat with alcohol - benzene (1 + 99) and alcohol - benzene (5 + 95), neither of which affects the dark band.

Identification of accelerators—This is accomplished by chromatography of the coloured solutions given

TABLE I

	M.B.T.	Z.D.C.	D.P.G.
Initial appearance of column	Grey zone at top	Green zone at top	Purple-violet zone immediately below the pink of the excess cobalt oleate
Development with (*a*) Benzene	Nil	Diffuse apple green zone passes rapidly down the column. Yellow and green zones remain at top of the column	Nil
(*b*) Absolute alcohol - benzene (1 + 99)	The grey ring splits into its components, the pink of cobalt oleate on top and the green due to M.B.T. below. On further washing, the green complex decomposes, the colour disappears, and M.B.T. passes out	Yellow zone developed slowly from the top of the column	Nil
(*c*) Absolute alcohol - benzene (5 + 95)	Development of M.B.T. continued	Yellow zone developed rapidly	Nil
(*d*) Absolute alcohol	Nil	Brown zone developed from the top. A green zone remains at the top of the column and is not eluted	Nil. The D.P.G.-cobalt oleate complex is not eluted

TABLE II

	D.P.G.	T.M.T.	Z.D.C.	M.B.T.	M.B.T.S.
Colour of solution	Deep blue	Deep green on standing	Green	Green	Blue (due to excess of reagent)
Initial appearance of column	Totally adsorbed as blue zone at top	Green zone with narrow brown zone at top	Green zone with yellow-brown zone near top	Blue zone at top	Dark blue zone (due to excess of reagent)
Development with (*a*) Benzene	Nil	Green zone with blue leading edge passes straight out	Green diffuse zone with blue edge moves out. Yellow zone moves very slowly	Nil	Nil
(*b*) Absolute alcohol - benzene (1 + 99)	Nil	Nil	Yellow zone developed which coalesces with that above and moves slowly	Green zone moves slowly down and fades in colour. Pure, colourless M.B.T. developed	Nil
(*c*) Absolute alcohol - benzene (5 + 95)	Nil	Brown zone at top eluted as pale yellow zone	Nil	M.B.T. development continued	Nil
(*d*) Absolute alcohol	Nil	—	Nil	—	Nil

with certain reagents. The following accelerators have been studied: tetramethylthiuram disulphide (T.M.T.); mercaptobenzthiazole (M.B.T.); zinc diethyldithiocarbamate (Z.D.C.); diphenylguanidine (D.P.G.); and dibenzthiazyl disulphide (M.B.T.S.).

Chromatography with (a) cobalt oleate—An excess of a 10 per cent. solution of cobalt oleate in benzene is added to a benzene solution of the accelerator and a chromatogram is made. Cobalt oleate is adsorbed as an inelutable pink zone at the top of the column. Results are given as Table I.

(*b*) *Uranyl nitrate*—This reagent reacts, after 1 hr. contact, only with the dithiocarbamates, giving with Z.D.C. an inelutable lemon-yellow zone adsorbed near the top of the column.

(*c*) *Cobaltous chloride*—Anhydrous cobaltous chloride is dissolved in absolute alcohol and diluted with as large a volume of benzene as is possible without precipitation. Results are given as Table II.

Scheme of identification—The following scheme is applicable to the identification of D.P.G., T.M.T., Z.D.C., M.B.T., and M.B.T.S., or their mixtures. (i) Remove Z.D.C. with uranyl nitrate on a column and elute the remaining accelerators with alcohol - benzene (5 + 95). (ii) Remove D.P.G. with cobalt oleate on a column. M.B.T. is detected as a green zone that decomposes on elution with alcohol - benzene. (iii) Remove T.M.T. with cobaltous chloride and wash the green zone through the column with benzene. Elute M.B.T. and M.B.T.S. with alcohol - benzene (5 + 95). (iv) Precipitate M.B.T. with lead oleate, make a chromatogram from the filtrate, and elute M.B.T.S. with alcohol - benzene. (v) Remove the solvent and then reduce any M.B.T.S. with magnesium and sulphuric acid. Extract with benzene and detect the resulting M.B.T. by method (iv) above. The alcohol is removed at each stage by evaporating down with benzene.

Identification of certain accelerators in vulcanisates—The vulcanisates examined contained only one accelerator and no anti-oxidant. The accelerator or its reaction products can be separated, in the way already described, from waxes, constituents of raw rubber, and stearic acid. M.B.T. was identified in the mix compounded with M.B.T.S., and Z.D.C. in that compounded with T.M.T. Caution is therefore necessary in giving the original components of a compound from an examination of the acetone extract of the vulcanisate. A very complex chromatogram is obtained from D.P.G. owing to the variety of its breakdown products. These appear to be characteristic of D.P.G., but D.P.G. itself was not identified among the products.

Parts IV and V—These deal with the characterisation of compounds used as anti-oxidants and describe their separation and identification in the material extractable from rubber vulcanisates.

Apparatus and materials—As for Parts I to III (above).

Identification of anti-oxidants—Anti-oxidants examined, with the exception of Flectol H (*vide infra*), are not strongly adsorbed on alumina and this exception is so rapidly eluted with alcohol - benzene (1 + 99) that there is no difficulty in separating anti-oxidants from components more strongly adsorbed on the column. Some difficulty may be met if complete separation of anti-oxidants from paraffin wax is required, but this can be accomplished by the use of a second column or an extra long column. In general, anti-oxidants do not give zones of distinctive colour, so that recourse to streak tests on the extruded column or spot tests on a tile is necessary for identification. Colour reactions with reagents are given in Table III.

Phenyl-α-naphthylamine (*P.A.N.*) fluoresces violet in ultra-violet light and its progress down the column can be followed in absence of interfering substances. Alternatively, the column can be extruded and

TABLE III

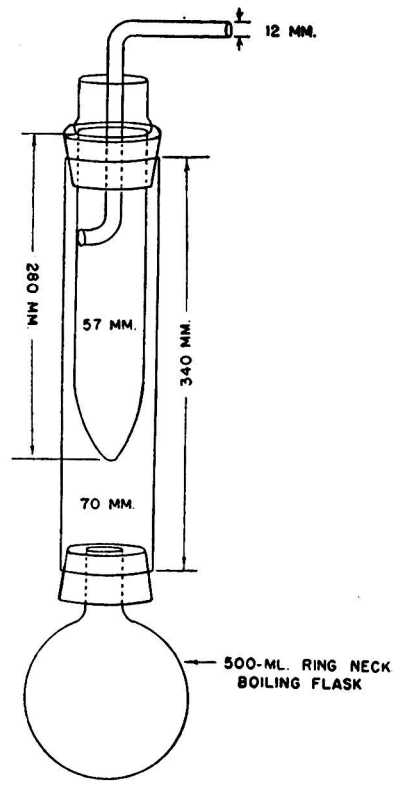
Anti-oxidants	Sulphuric acid	1 per cent. Ammonium vanadate in sulphuric acid	1 per cent. Potassium dichromate in sulphuric acid	Nitric acid - sulphuric acid mixture (1 + 3)
Phenyl-α-naphthylamine	Faint green	Vivid green	Green-blue	Green
Phenyl-β-naphthylamine	Pale yellow	Very faint green-yellow	Brown-green	Red
Agerite White	Green	Prussian blue	Red, changing to Prussian blue	Purple
Flectol H	Nil	Faint red-brown	Faint red-brown	Bright red
Agerite Stalite	Nil	Nil	Strong brown-ochre	Green
B.L.E.	Nil	Green	Green	Deep violet
Nonox S	Faint brown-green	Brown	Nil	Brown
Neozone H.F.	Brown-green	Emerald green	Red, changing to emerald green	Red

streaked with the ammonium vanadate reagent. *Phenyl-β-naphthylamine* (*P.B.N.*) also fluoresces in ultra-violet light and cannot be separated from P.A.N. on an ordinary column, but can be distinguished from P.A.N. by streaking the extruded column with the nitric acid reagent. *Agerite White* (stated to be *sym*-NN′-dinaphthylphenylenediamine), in addition to its blue fluorescence in ultra-violet light and the use of streak reagents, can be distinguished by the strong purple tinge it develops on standing in light. On making a chromatogram of this exposed material, the bulk of the Agerite White passes through with benzene, but now has a pink zone with a strong purple trailing edge. In addition, a bright light blue zone remains fixed at the top of the column. *Neozone HF* is a complex mixture identifiable by streak tests on the extruded column. *Flectol H*, an acetone - aniline condensation product, is exceptional as it is not eluted with benzene. The bulk of it is eluted with alcohol - benzene (1 + 99) as a narrow brown zone travelling at the same speed as the solvent front, and a small fraction with absolute alcohol, as a pale blue zone. *Agerite Stalite* is also a complex mixture that, in benzene solution, gives some fluorescence in ultra-violet light. The bulk of the material passes through the column with benzene, leaving secondary zones requiring elution with more polar solvents. *B.L.E.*, an anti-oxidant of unstated composition, shows a green fluorescence in benzene and is adsorbed on the column as a black band at the top with a light brown zone below. Development with benzene elutes a pale yellow zone containing the bulk of the material. The other zones seem to indicate the presence of impurities. These anti-oxidants were incorporated singly into two series of rubber compounds, one series accelerated with mercaptobenzthiazole, the other with diphenylguanidine, and examination of the acetone extract dissolved in benzene showed that the anti-oxidant could be separated from the other compounds, including the accelerator, and could be identified on and recovered from the column. W. C. WAKE

Apparatus for Low-temperature Drying. F. J Reithel (*J. Chem. Educ.*, 1947, **24**, 286)—The apparatus shown in the figure is simple, inexpensive, and efficient, thus enabling its use to extend beyond research products. The No. 13 rubber stopper at the top is bored with a piece of iron pipe turned down to the correct dimensions. The outlet tube passes through the bath of alcohol and "dry-ice." The ring neck of the 500-ml. boiling flask had been removed before insertion through the stopper.

Procedure—Half fill the inner tube with ethanol, and add dry-ice until excessive ebullition ceases. During this time, add 50 to 100 ml. of the solution to be dried to the flask, inserted in its stopper, and freeze it in a thin layer on the walls by rotating in an alcohol - dry-ice bath until a slight snapping sound is heard. Then insert the stopper into the large tube and apply a Hyvac vacuum pump at the outlet tube.

Although the stoppers do not permit maximum reduction of pressure being obtained, a 50-ml.



portion of 2 per cent. protein solution was dehydrated in 3 hr. M. E. DALZIEL

Examination of Absolute and Comparative Methods of Polarographic Analysis. J. K. Taylor (*Anal. Chem.*, 1947, **19**, 368–372)—Absolute methods of polarographic analysis involve the use of the Ilkovič equation. For analytical purposes, the usefulness of this equation is increased by the application of the diffusion current constant (*cf.* Lingane, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 658), $I = knD^{1/2} = i_d/Cm^{2/3}t^{1/6}$, where I is the diffusion current constant, i_d the diffusion current, m is the mass of mercury flowing from the capillary in unit time, t is the drop time, D is the diffusion coefficient, C the concentration of the reducible or oxidisable substance, n is the number of electrons involved in the electrode reaction, and k is a constant. The value of I is constant for a given ion under given experimental conditions, and if the values of the terms in the above equation are known, a quantitative analysis of any substance the diffusion current constant of which is known can be carried out without the use of calibration curves. Accurate analyses by this method involve careful and accurate measurements of the terms of the equation. The values of the terms should not be seriously affected by the conditions of the actual determination.

Many of the difficulties in the absolute method can be eliminated or minimised by the use of a comparative method. The simplest comparative method involves the preparation of a calibration curve relating wave-height to the concentration of the substance under examination. In the "Pilot Ion" method, the ratio of the diffusion current of the ion to be determined to that of a known amount of some standard ion added to the solution is measured, and this ratio is taken as being proportional to the concentration of the former ion. This method is not usually applicable where several ions are to be determined simultaneously. A third comparative method involves the measurement of the diffusion current of a solution containing the ion to be determined before and after the addition of a known amount of the same ion. In this way, the standardisation is carried out under conditions that are almost identical with those of the analysis. In some analyses, particularly in the examination of certain alloys, standard samples are available, and these can be run along with the samples under examination, comparison of the wave-heights giving the desired result.

Finally, use can be made of a semi-comparative method, whereby the experimental conditions for each determination are observed, and the results are corrected for variations in these conditions by means of the Ilkovič equation. J. G. WALLER

Reviews

CHEMISTRY IN THE SERVICE OF MAN. By ALEXANDER FINDLAY. Seventh Edition. Pp. xx + 390. London, New York, Toronto: Longmans, Green & Co., Ltd. 1947. Price 12s. 6d.

Reviews of earlier editions of this book have appeared in THE ANALYST (1931, **56**, 843; 1940, **65**, 535), and the present edition needs little further comment.

In the preface to the first edition (1916) of this book, Professor Findlay observed that "The mental outlook and the attitude of the people as a whole towards science must be changed and the scientific habit and a spirit of trust in science must be cultivated"; in the present edition he points out that much progress has been made towards the attainment of these ends.

The progress of science, recorded in scientific journals and ultimately in textbooks, is written for students of science and usually in language unintelligible to any but students of science. The author's book bridges the gap that confronts the general reader, and the fact that it has reached a seventh edition in 31 years is evidence that it has contributed in no small degree to the increased value now attached, in the public mind, to chemical science. The advance of chemical science during this period, both in theory and in practical application, has been spectacular, more particularly as applied in medicine, surgery and agriculture, and above all in the field of atomic chemistry. Professor Findlay's book gives the general reader a very clear epitome of the progress that has been made in these and other branches of applied chemistry, and it can be strongly recommended for its great educational value. LEWIS EYNON

VOLUMETRIC ANALYSIS. By I. M. KOLTHOFF and V. A. STENGER. VOLUME II—TITRATION METHODS: ACID-BASE, PRECIPITATION AND COMPLEX-FORMATION REACTIONS. Pp. xiii + 374. New York and London: Interscience Publishers Inc. 1947. Price 36s. 0d.

Twenty years ago, Professor Kolthoff, in collaboration with Dr. H. Menzel, of Dresden, wrote a book entitled "*Die Praxis der Massanalyse*," which was translated into English by Dr. N. H. Furman, and was published in two volumes a year later. The popularity at that time of books on volumetric analysis by Sutton and by Treadwell and Hall, together with the more academic treatment given to the subject by Kolthoff, may have been responsible for the fact that this translation became less widely known and used in this country than it deserved to be. The first two volumes of the second edition have now been published, this time with V. A. Stenger of the Dow Chemical Company, at Michigan, as translator and collaborator.

Professor Kolthoff has always supported the claims of volumetric over gravimetric methods of analysis, and the work that he and his students have carried out over a long period at the University of Minnesota has done much to correct the view that volumetric methods are necessarily less accurate than those of gravimetric analysis. The wide range covered by the original investigations of his school enables him to write authoritatively on volumetric analysis and to make a critical selection of methods in this volume, which deals with the practice and application of titration methods to the determination of organic as well as inorganic substances. The limitations of a given method and information on its precision and accuracy, often the result of first-hand knowledge, can also be, and are, given. This is usually done as notes following the procedure describing a particular determination, and in these the reader will find much that is interesting and useful.

The subject-matter of the book is arranged on what may be called physico-chemical lines, and in this sense the treatment is more academic than might be expected in a book dealing with the practice of volumetric analysis. The procedures laid down are arranged according to the type of reaction involved in them rather than to the field in which they are applied. For this reason the work may appeal more to the research chemist than to a busy practising analyst, but the reader who would prefer a more utilitarian arrangement of the subject-matter will find compensation in a good index.

So far as one can judge, the work of revision has been done well, and, although the authors are careful to point out that the volume does not include a complete discussion of work done outside America since 1940, the text is quite well supported by references to papers published since that time. Future editions,

however, should contain at least a reference to the latest modifications by Parnas (*Z. anal. Chem.*, 1938, **114**, 261) of the Parnas-Wagner apparatus for determining micro-amounts of ammonia now designed to deal with macro-quantities in much less time than is usually required in a Kjeldahl distillation. Pugh's method (*J. Chem. Soc.*, 1937, 1824) for titrating chloride or bromide with mercurous perchlorate solution, bromophenol blue being used as an adsorption indicator, an excellent example of the use of an indicator of this type, should also be mentioned.

Since the first edition of this book appeared so much new work has been published that a third volume, promised for the end of this year, is needed to deal with oxidation - reduction reactions, and the volume being reviewed has been limited to titrations involving acid - base, precipitation, and complex-formation reactions. The early chapters contain much of general interest about volumetric apparatus and methods, the sections dealing with the draining of burettes and the requirements for primary and secondary standard materials, and especially the sections that describe primary substances for the standardisation of acids and of alkalis, being particularly interesting and valuable. In fact, this book is one of the few places where essential information on the preparation and critical examination of many of the pure substances needed in volumetric analysis is easily available for reference in a single volume. The information given about indicators, particularly mixed and screened indicators, which might well be used more than they are, is also a commendable feature of the book. We also learn of experiments, not yet published, indicating that thermal hysteresis effects in glassware are smaller than hitherto supposed; they may well prove to be negligible for analytical purposes. Readers will be less ready to accept the statement (p. 31), concerning the preparation of a standard solution by the dissolution of a weighed quantity of solid and accurate dilution, that "it is good practice to invert the flask from thirty to forty times."

It is a pity that this book which, in many ways, is so good, is not better produced. The printing of the text and the quality of the paper are only adequate—they do not reach the standard of the first edition—and the proof-reading leaves much to be desired. Better editing would have removed many minor blemishes to improve the volume.

The book deserves to be widely read and used. It can be recommended to all analytical chemists, especially to those who want to know how much guidance and help physical chemistry has to give in the selection and use of volumetric methods of analysis. L. S. THEOBALD

BIOLOGICAL METHODS GROUP

A MEETING of the Group will be held in the Rooms of The Chemical Society, Burlington House, Piccadilly, London, W.1, on Tuesday, May 11th, at 6.30 p.m. Dr. A. A. Miles, Head of the Department of Biological Standards, National Institute for Medical Research, will read a paper on "Biological Standards." Visitors are welcomed at meetings of the Group.

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