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Editor: J. H. LANE, B.Sc., F.R.I.C.
7-8, IDOL LANE, LONDON, E.C.3
Telephone: MANsion House 6608

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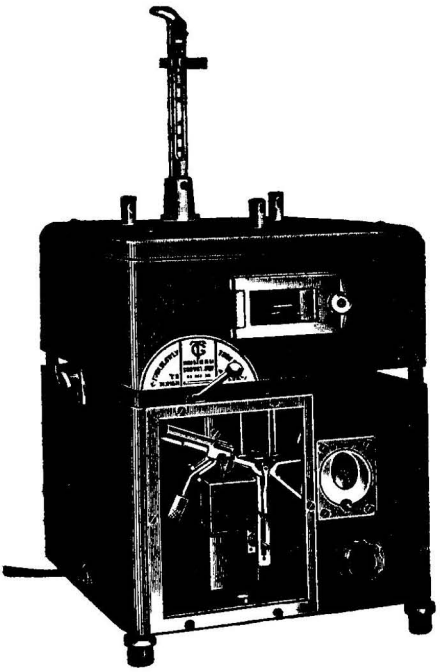

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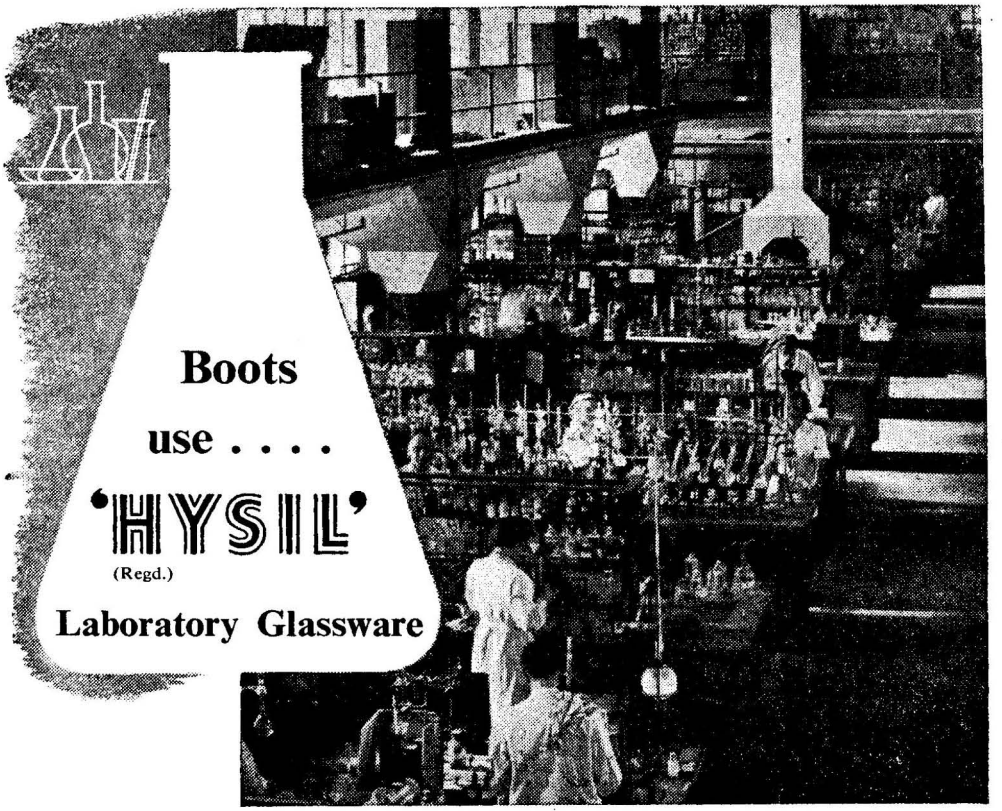

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THE ANALYST

EDITORIAL

THE ANALYST FOR 1950

THE changes in the contents of *The Analyst* that begin in this issue call for some explanation. To readers familiar with the journal the most striking and perhaps the most debatable, is the disappearance of the abstracts section. The increase in the amount of space occupied by original papers was to be expected, and was indeed overdue in view of the arrears to be cleared off and the increasing number of papers received for publication. But the need for more space for original papers was not the main reason for discontinuing the abstracts. The considerations mentioned below were the determining factors.

From its early years *The Analyst* has given particular attention to making its abstracts as useful as possible to the general analyst at the laboratory bench. After the establishment of the large abstract services with their comprehensive collections of "indicative" abstracts, *The Analyst* concentrated particularly on producing a selected set of abstracts of the more important analytical papers in a form directly applicable at the bench, without the necessity for reference to the original papers. To many analysts, particularly those without ready access to chemical libraries, these abstracts proved very useful; some readers have indeed described *The Analyst* as a "running textbook of analytical chemistry."

This state of affairs remained satisfactory so long as most analytical methods were of the relatively simple classical techniques which did not require long descriptions and highly specialised knowledge. In recent years, however, the number and complexity of analytical problems have so greatly increased, and so many highly specialised techniques have been pressed into the service of analysis, that the production of "working abstracts" of many present-day papers is not practicable within reasonable length. Recent experience has convinced the Council of the Society that it is no longer justifiable to devote the necessary labour, expense and printing space to the production of "working abstracts," which cannot efficiently perform for modern methods what the same system did successfully for the simpler techniques of the past.

The Council has therefore decided to cease the publication of abstracts in *The Analyst* and, by arrangement with the Bureau of Abstracts, to supply all members of the Society and all non-member subscribers to the journal, with the set of analytical abstracts known as "Abstracts C (Analytical and Apparatus)." These are already published by the Bureau in a form separate from their other abstracts. "Abstracts C" are in general less detailed than those hitherto published in *The Analyst*, but they provide a comprehensive survey of publications on analytical chemistry; and, for that reason, should prove to be more acceptable and more generally useful to the majority of our readers than did the limited abstract service hitherto supplied.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry was held at 3.45 p.m. on Tuesday, December 6th, 1949, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1. The meeting was in two sessions, the President of the Society, Mr. George Taylor, O.B.E., F.R.I.C., taking the Chair in the afternoon, and Mr. A. L. Bacharach, M.A., F.R.I.C., Chairman of the Food Group, taking the Chair in the evening.

The subject of the meeting was "Properties of Pectin and its Use in the Food Industry," and the following papers were presented and discussed: "Chemical Composition and Properties of Pectin," by J. K. N. Jones, D.Sc., A.R.I.C.; "Laboratory Assessment of Pectin Quality with Special Reference to Jelly Grading," by Miss M. Olliver, M.Sc., F.R.I.C.; "Distribution, Sources and Manufacture of Pectin," by V. L. S. Charley, B.Sc., Ph.D.; "Industrial Uses of Pectin," by R. W. Money, M.Sc., F.R.I.C.

NEW MEMBERS

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The Determination of Chromium in Chromite* Part I. Volumetric Determination of Chromate with Special Reference to the Effects of Vanadate and Arsenate

BY W. FURNESS†

SYNOPSIS—Various forms of the titrimetric determination of chromate by reduction with ferrous ammonium sulphate solution are considered with reference to their use as the final step in the determination of chromium in chromite. In the reduction of pure chromate with the ferrous solution and back-titration with permanganate solution, the use of various redox indicators (disulphine blue, barium diphenylamine sulphonate, N-phenyl anthranilic acid or ferroin), or no indicator at all, gave equally accurate results (mean error ±0·03 per cent.). Vanadic acid, but not arsenic acid, interferes. This interference can be avoided by use of nitroferroin as indicator, with higher acidity in the solution. In the direct titration of chromate with ferrous ammonium sulphate solution (standardised against permanganate and this against sodium oxalate or arsenious oxide) positive errors, *e.g.*, 0·3 per cent. were obtained. Satisfactory reproducibility may be obtained by reducing the chromate with excess of ferrous ammonium sulphate solution and titrating back with dichromate solution. To ensure accuracy in this procedure potassium dichromate must be taken as primary standard, and the conditions specified for titration in the assay must be reproduced in the standardisation. Vanadium, however, interferes.

* During 1944 the Chrome Ore, Magnesite and Wolfram Control of the Ministry of Supply had occasion to review methods for determining the chromium content of chrome ores in common use at that time in this country. A small committee representing various interested Government Departments was formed by the Controller of Chemical Research and Development, Ministry of Supply, to explore the possibilities of co-ordinating the various methods of analysis in use. A memorandum was circulated to seven Government Departments and to fifty-three metallurgical firms, or firms of analysts, asking for their views, and as a result many descriptions of current methods (some of which showed considerable divergencies) and helpful suggestions were received. These contributions are gratefully acknowledged. As there was clearly a certain amount of doubt about the simplest and most reliable procedure at various stages, it was decided to undertake the investigation now reported. This and the following papers describe the contributions made by representatives (F. J. B., W. F.) of the Chemical Inspectorate of the Ministry of Supply, and by a representative (P. J. H.) of the Department of the Government Chemist.

† Present address—Brotherton and Co., Ltd., Central Research Department, Kirkstall Lane, Leeds 5.

INTRODUCTION—Methods proposed for quantitatively converting the chromium content of the mineral chromite into soluble chromate fall into two main groups—

(i) *Solution methods*: dissolution of the sample in 70 per cent. perchloric acid, the same acid being used at the boiling-point as oxidant[1]; or dissolution and oxidation by means of a mixture of sulphuric and perchloric acids[2]; or dissolution in a mixture of sulphuric and phosphoric acids, perchloric acid being used as principal oxidant but followed by permanganate.[3]

(ii) *Fusion methods*: fusion with alkaline oxidising fluxes based on sodium peroxide[4,5,6] and extraction of the melt, followed by an auxiliary oxidation, *e.g.*, with silver nitrate and persulphate in acid solution.[4,5]

Methods of the first group provide the only practicable means whereby chromite minerals can be dissolved completely in aqueous solvents. However, the use of perchloric acid as oxidant for chromium received a set-back in 1931 when Lundell, Hoffman and Bright[7] pointed out that oxidation by that reagent alone was rarely more than 99·5 per cent. effective. This was later attributed to partial reduction of chromic acid by traces of hydrogen peroxide resulting from decomposition of the perchloric acid, but improvements in procedure since recommended by Smith and others[2,3,8] have largely offset this drawback. Nevertheless, methods depending on perchloric acid as oxidant are not commonly employed in this country for the assay of chrome ores.

Methods of the second group are generally employed when only the chromium content of the ore is required. The best known procedures are those of Hillebrand and Lundell[4] and of Cunningham and McNeill.[5] In the former method chromium is separated from iron by filtration of the aqueous extract of the melt and the insoluble matter is returned for a second fusion; in the latter method a single fusion only is made and the melt extracted with dilute acid, so that chromium and iron are brought into solution together. Both authorities recommend an auxiliary process of oxidation to ensure complete conversion of chromium to the sexavalent condition, after which an excess of ferrous ion is added and the excess determined by titration with permanganate.

The present investigations relate primarily to methods of the second group, and the results are being reported in three parts. In this, the first part, difficulties of the titration procedure are discussed with special reference to the choice of primary standards, satisfactory indicators, and the development of a procedure applicable in presence of vanadate and arsenate. There follows in Part II a study of methods for the determination of chromium in the melts obtained by fusion of mixtures of potassium dichromate with certain metallic oxides in alkaline fluxes containing sodium peroxide. Finally, in Part III, a selected procedure for the analysis of chromite is described and tested by reference to the U.S. National Bureau of Standards Chrome Refractory No. 103.

VOLUMETRIC PRIMARY STANDARDS—The following standard reagents, maintained at 18° to 20° C. throughout the investigation, were used.

Potassium dichromate—Willard and Gibson[1] observed that potassium dichromate of C.P. grade may contain excess of chromic acid. However, in the present investigation the chromate content of a specimen of AnalaR potassium dichromate was not significantly changed on re-crystallising twice from water. A solution standardised as follows was therefore accepted as one of the primary standards.

The solution contained approximately 0·50 g. of re-crystallised potassium dichromate per 50 ml. The actual weight of potassium dichromate delivered by a 50-ml. pipette at 20° C. was determined by emptying the pipette into a tared platinum dish, evaporating, and heating at 150° C. to constant weight. Three checks (0·5046 g., 0·5047 g., 0·5044 g., mean 0·5046 g., for example) showed what variation might be expected between successive deliveries from that pipette.

Potassium permanganate—The decinormal solution was standardised on alternate days, but no significant variation was detected during three weeks. Two primary standards were used, *viz.*, dried AnalaR sodium oxalate (procedure of Fowler and Bright[9]), and dried AnalaR arsenious oxide (procedure of Metzler, Myers and Swift[10]).

Ferrous ammonium sulphate—The approximately decinormal solution of this salt in diluted sulphuric acid (1 in 10) was standardised afresh at the time of use by the appropriate methods given below.

Determination of chromate by reduction with excess of ferrous ion followed by back-titration with permanganate

In the absence of vanadate the chief indicators already available for this titration are:

(*a*) the colour due to excess of permanganate;
(*b*) disulphine blue, 0·1 per cent. aqueous solution;
(*c*) barium diphenylamine sulphonate, 0·3 per cent. aqueous solution;
(*d*) N-phenyl anthranilic acid, 0·1 per cent. in 0·1 per cent. sodium carbonate solution;
(*e*) 1 : 10-phenanthroline ferrous sulphate (Ferroin) solution, 0·025 *N*.

The following tests were made with each indicator to simulate the conditions that would obtain in an actual analysis of chromite—

0·5046 g. of potassium dichromate, delivered by pipette into 500 ml. of 2 *N* sulphuric acid, was reduced with 100 ml. of approximately 0·106 *N* ferrous ion. Using each indicator in turn, and with 25 ml. of phosphoric acid in cases (*a*), (*b*) and (*c*), the excess of ferrous ion was titrated with standard decinormal permanganate. Concurrently, 100 ml. of the ferrous ion solution in 500 ml. of 2 *N* sulphuric acid were titrated with the decinormal permanganate, using the respective indicators and with phosphoric acid as before. Assuming that indicator blanks cancel, the results of duplicated titrations were calculated and are set out in Table I.

Table I

0·5046 g. of potassium dichromate taken in each case

Indicator	Permanganate equivalent ml. 0·10103 *N*	Potassium dichromate found, g.	Error g.
a	104·90 − 3·05 = 101·85	0·5046	0·0000
a	104·90 − 3·00 = 101·90	0·5048	+ 0·0002
b	104·75 − 2·87 = 101·88	0·5047	+ 0·0001
b	104·75 − 2·95 = 101·80	0·5043	− 0·0003
c	105·08 − 3·28 = 101·80	0·5043	− 0·0003
c	105·05 − 3·26 = 101·79	0·5043	− 0·0003
d	104·63 − 2·74 = 101·89	0·5048	+ 0·0002
d	104·65 − 2·78 = 101·87	0·5047	+ 0·0001
e	104·65 − 2·78 = 101·87	0·5047	+ 0·0001
e	104·65 − 2·80 = 101·85	0·5046	0·0000

The end-points with barium diphenylamine sulphonate (*c*) and ferroin (*e*) were the most easily distinguishable. With N-phenyl anthranilic acid (*d*) and disulphine blue (*b*) the end-points were less sharp. Without any added indicator (*a*), the troublesome procedure of comparing the deep blue-green colour of the solution in the region of the end-point with that of another solution containing an equivalent amount of chromic sulphate had to be adopted. In each case the accuracy of the results is seen to be very nearly as good as the precision with which the pipette delivered the standard dichromate solution.

In other similar experiments 5 ml. of 0·100 *N* potassium arsenate were introduced before the addition of excess of ferrous ion. No interference ensued in the determination of dichromate.

In the presence of vanadate, however, interference was encountered. Vanadate is quantitatively reduced by ferrous ion to the vanadyl state and re-oxidation with decinormal permanganate is rather slow, especially towards the end of the reaction, if it is carried out in 2 *N* sulphuric acid at 20° C. Willard and Young[11] showed that the oxidation of vanadyl ion proceeds more rapidly at elevated temperatures (40° to 50° C.), especially in solutions of higher pH such as may be obtained by buffering with sodium acetate. Oxidation is also accelerated in presence of phosphoric acid. However, no simple modification of procedure along these lines alone afforded results for chromate comparable in accuracy with those reported in Table I. Barium diphenylamine sulphonate and N-phenyl anthranilic acid are not applicable, of course, because in presence of vanadate both indicators assume their oxidised forms. Nor is disulphine blue satisfactory, for in the final stages of the back-titration there is a pronounced lag due to a slow reaction between the oxidised form of the indicator and vanadyl ion.

To facilitate observation of the equivalence-point in such circumstances, Willard and Young (*loc. cit.*) used ferroin, but mentioned that this indicator suffers decomposition at temperatures above 50° C. All specimens of ferroin used by the present author showed

distinct signs of decomposition at 40° C. and observation of the colour change was consequently impaired. On the other hand, at temperatures below 40° C. the action of the indicator is sluggish, for in the conditions just preceding the equivalence-point, the oxidised form of the indicator is able to oxidise vanadyl ion only very slowly.

The practicability of substituting 5-nitro-1 : 10-phenanthroline ferrous sulphate (Nitroferroin), an indicator of higher redox potential, for the determination of dichromate in the presence of vanadate has therefore been investigated.

When introducing this indicator in 1934, Hammett, Walden and Edmonds[12] observed that in *M* sulphuric acid solution it did not appear to be oxidised in presence of vanadic acid, but in titrations of ferrous ion with ceric ion it did not give a sharp end-point. This indicator was later used by Smith and Getz[13] in cerate oxidimetry for titrations of oxalate and arsenite, and has been further described by Smith and Richter.[14,15]

Now the formal oxidation - reduction potentials of the systems $MnO_4'/Mn^{\cdot\cdot}$, $VO_4'''/VO^{\cdot\cdot}$, nitroferroin/nitroferroin in sulphuric acid solution depend on the concentration of this acid. The relative values of these formal potentials, and that of the ferric/ferrous system in sulphuric acid solutions up to 9 *N* concentration, are shown approximately in Fig. 1. Data for the indicator and for the vanadate/vanadyl system are taken from Smith and Richter.[14,15]

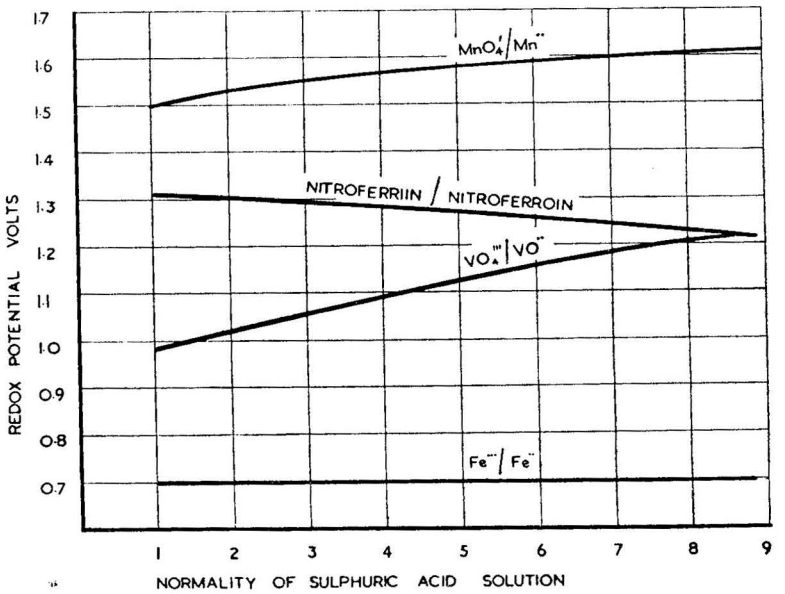

Fig. 1

From these data it may be expected that in a direct titration of ferrous ion with permanganate the precision and accuracy of the end-point as indicated by nitroferroin should improve as the normality of the sulphuric acid is raised. On the other hand, whilst nitroferroin is easier to oxidise at the higher acid concentrations, oxidation of vanadyl ion becomes increasingly more difficult until in 8 *N* or 9 *N* sulphuric acid the formal oxidation - reduction potentials of the two systems are approximately equal. In other words, when ferrous ion alone is being titrated with permanganate one may expect to observe the sharpest indicator reaction at the higher acidities, but if vanadyl ion has to be completely oxidised before nitroferroin changes appreciably to its oxidised form, lower acidities should be more favourable. The possibility of successfully titrating ferrous and vanadyl ions together, using nitroferroin as indicator, therefore rests on a satisfactory compromise between the two opposing factors.

In order to arrive at such a compromise two series of titrations were carried out at 20° C. In each series 25·00 ml. of approximately 0·1 *N* ferrous ion in 300 ml. of sulphuric acid solution, which varied in concentration throughout the series from 1 *N* to 6 *N*, were titrated with standard decinormal permanganate, 0·1 ml. of 0·025 *N* nitroferroin being added as indicator. In one series, however, 1·00 ml. of 0·100 *N* ammonium vanadate solution was added; the other series contained no vanadate. Table II summarises the results.

TABLE II

Normality of sulphuric acid	Titration of 0·1 *N* ferrous ion in absence of vanadate (Note 1)		Titration of 0·1 *N* ferrous ion in presence of 1·00 ml. 0·100 *N* vanadate	
	ml.	End-point	ml.	End-point
1	23·5–24·0	very indistinct	23·5–24·5	very indistinct
2	23·7–23·9	indistinct	23·9	indistinct
3	23·85	fairly sharp	23·84	fairly sharp
4	23·83	sharp	23·84	distinct (note 2)
5	23·82	extremely sharp	23·82	distinct (note 3)
6	23·83	extremely sharp	23·80	distinct (note 4)

NOTE 1—Using ferroin as indicator in a control titration, 25·00 ml. of the ferrous ion solution in 300 ml. of 2 *N* sulphuric acid required 23·82 ml. of the same permanganate solution.

NOTE 2—In approaching the end-point the last 0·5 ml. of permanganate solution required 5 minutes to react.

NOTE 3—In approaching the end-point the last 0·5 ml. of permanganate solution required 8 minutes to react.

NOTE 4—In approaching the end-point the last 0·5 ml. of permanganate solution required 10 minutes to react.

In absence of vanadium the sensitivity of the colour change (orange to pale grey-blue) in sulphuric acid of concentration 5 *N* or 6 *N* is at least as good as that of any other indicator so far investigated. On the other hand the oxidation of vanadyl ion is inconveniently slow in sulphuric acid of concentration greater than 4 *N*, but a good end-point, which coincides very closely with the true equivalence point, can be reached readily in 3 *N* or 4 *N* sulphuric acid.

In most analyses of chromite samples, the amount of vanadium encountered will generally be less than the equivalent of 1 ml. of decinormal vanadate solution, and for such purposes it is suggested that nitroferroin will be most useful in a sulphuric acid solution of concentration 4 *N*. Further experiments, using nitroferroin as indicator, were made along the same lines as those which gave the results reported in Table I, except that in some instances ammonium vanadate was added to the potassium dichromate before reduction with excess of ferrous ion. The precise procedure was as follows—

(i) *Standardisation of ferrous ammonium sulphate solution*—100 ml. of the solution, which was approximately 0·12 *N*, were transferred by pipette to a 1000-ml. flask, 400 ml. of 5 *N* sulphuric acid were added (so that the concentration of sulphuric acid would finally be approximately 4 *N*) and the solution was titrated with the standard decinormal permanganate until within about 5 ml. of the equivalence-point. Then 0·2 ml. of 0·025 *N* nitroferroin indicator was added and the titration continued to the end-point.

(ii) *Determination of potassium dichromate*—0·5009 g. of potassium dichromate in solution was transferred by 50-ml. pipette to a 1000-ml. flask. Various volumes (from 0 to 2·0 ml. in different experiments) of 0·100 *N* ammonium vanadate were introduced, the solution was diluted to 100 ml. with water and then 400 ml. of 5 *N* sulphuric acid were added. 100 ml. of the ferrous ammonium sulphate solution were added, followed by 0·2 ml. of 0·025 *N* nitroferroin indicator, and the excess of ferrous ion was titrated with the standard decinormal permanganate solution.

TABLE III

0·5009 g. of potassium dichromate taken in each case

0·100 *N* vanadate added	Permanganate equivalent	Potassium dichromate found	Error
ml.	ml. of 0·10120 *N* $KMnO_4$	g.	g.
nil	118·50 − 17·56 = 100·94	0·5009	0·0000
nil	118·50 − 17·60 = 100·90	0·5007	− 0·0002
0·5	118·50 − 17·58 = 100·92	0·5008	− 0·0001
0·5	118·50 − 17·58 = 100·92	0·5008	− 0·0001
1·0	118·46 − 17·51 = 100·95	0·5009	0·0000
1·0	118·46 − 17·48 = 100·98	0·5011	+ 0·0002
2·0	118·46 − 17·48 = 100·98	0·5011	+ 0·0002
2·0	118·46 − 17·50 = 100·96	0·5010	+ 0·0001

The results are recorded in Table III. In no case was there any undue delay in the final stages of the permanganate titration, and the colour change of the indicator, although superimposed on the deep blue-green colour of the chromic sulphate, was clearly observed and found to be very stable. The introduction of 5 ml. of 0·100 *N* potassium arsenate caused no interference.

Determination of chromate by direct titration with standard ferrous ammonium sulphate solution

Using an electrometric method of titration, Eppley and Vosburgh[16] showed that under certain conditions potassium dichromate appeared to oxidise more than its equivalent of ferrous ion. Titrating 25 ml. of 0·1 *N* dichromate in 250 ml. of 2 *M* hydrochloric acid solution with 0·1 *N* ferrous sulphate standardised against permanganate, an excess of ferrous ion above the theoretical amounting to from 0·3 to 0·5 per cent. was required. Similarly, in the reverse titration of standard ferrous sulphate solution with dichromate, a 0·10000 *N* dichromate solution appeared to have a normality of 0·10037. Willard and Gibson[1] have also reported inconsistencies in electrometric titrations of dichromate with ferrous ion as the acidity and concentration of the dichromate solution were varied.

The following experiments were therefore undertaken to decide whether inaccuracies might also arise in the direct titration of dichromate with ferrous ion standardised against permanganate, using the indicators (*a*) barium diphenylamine sulphonate, (*b*) N-phenyl anthranilic acid, (*c*) ferroin. In view of the results obtained the procedures are described in detail.

(i) *Standardisation of ferrous ammonium sulphate solution*—50 ml. of decinormal permanganate, standardised by the two methods mentioned on p. 3, were added to 100 ml. of 2 *N* sulphuric acid. The ferrous ammonium sulphate was immediately titrated into the acidified permanganate solution, and, when near the equivalence-point, in one series 10 ml. of phosphoric acid (sp.gr. 1·75) and 2 drops of barium diphenylamine sulphonate indicator were added, and in the other series 2 drops of ferroin indicator alone were added. Titration was then continued to the end-point. The two series of titrations gave the values 0·10664 and 0·10662, the mean, 0·10663, being accepted for the normality of the ferrous ion solution.

(ii) *Determination of potassium dichromate*—0·5046 g. of potassium dichromate was transferred by 50-ml. pipette (*cf.* p. 3) to a flask containing 400 ml. of 2 *N* sulphuric acid. The dichromate was titrated with the freshly standardised ferrous ion solution until within a few ml. of the equivalence-point. The appropriate indicator was added, together with 25 ml. of phosphoric acid in the case of indicator (*a*), and the titration continued to the end-point.

The end-point was distinct with indicators (*a*) and (*b*), but ferroin was less satisfactory in this procedure. Single titrations only were made with each indicator, and the results, calculated on the assumption that indicator blanks in the standardisation cancel those in the determination, are recorded in Table IV opposite indicators a_1, b_1, c_1.

(iii) *Repetition of titrations*—On the next day the ferrous ion solution was re-standardised, on this occasion by titration *with* the standard decinormal permanganate, using ferroin and correcting for the indicator blank. The determination of dichromate was repeated with appropriate corrections for indicator blanks, and the figures shown in Table IV opposite indicators a_2, b_2, c_2 were obtained.

The standardisation of ferrous ion solution and titrations of dichromate were again repeated. Now each indicator was prepared in the "just reduced" form, *i.e.*, in separate small beakers the amount of indicator required was first oxidised with dichromate in dilute sulphuric acid solution, then just converted to its fully reduced form with 0·01 *N* ferrous sulphate before being added to the titration flask. The results are shown opposite a_3, b_3, c_3 in Table IV.

All the results shown in Table IV are high, the mean error being +0·0016 g. Hardwick,[17] working independently, also observed under similar conditions a discrepancy of +0·0018 g. in the titration of 0·5 g. quantities of potassium dichromate with ferrous ammonium sulphate solution standardised against permanganate. It is considered that these errors are too large to be attributed entirely to manipulative or calibration errors.

Amounting approximately to 0·3 per cent., they are of the same sign and magnitude as the error recorded by Eppley and Vosburgh.

TABLE IV

0·5046 g. of potassium dichromate taken in each case

Indicator	Ferrous ion titration	Potassium dichromate found g.	Error g.
a_1	96·80 ml. 0·10663 *N*	0·5061	+ 0·0015
b_1	97·03 ml. 0·10663 *N*	0·5073	+ 0·0027
c_1	96·94 ml. 0·10663 *N*	0·5069	+ 0·0023
a_2	98·03 ml. 0·10529 *N*	0·5061	+ 0·0015
b_2	98·00 ml. 0·10529 *N*	0·5060	+ 0·0014
c_2	97·98 ml. 0·10529 *N*	0·5059	+ 0·0013
a_3	97·95 ml. 0·10521 *N*	0·5053	+ 0·0007
b_3	98·03 ml. 0·10521 *N*	0·5059	+ 0·0013
c_3	98·08 ml. 0·10521 *N*	0·5060	+ 0·0014

For the purposes of chrome ore analysis it is possible that the error could be eliminated by standardising the ferrous ion against pure potassium dichromate. Such a procedure would not, however, be entirely free from objection, and until fresh evidence can be produced misgivings must arise in connection with this method for determining chromium.

The presence of arsenate does not, apparently, influence the result obtained for chromate, but in the presence of vanadate the method is not applicable.

DETERMINATION OF CHROMATE BY REDUCTION WITH EXCESS OF FERROUS ION FOLLOWED BY BACK-TITRATION WITH DICHROMATE

In applying this procedure to the analysis of chromite the purest available potassium dichromate is conveniently accepted as the primary standard. The ferrous ammonium sulphate solution is accordingly standardised by titration *with* a primary standard potassium dichromate solution. However, in view of the observations of Eppley and Vosburgh[16] and in accordance with the suggestions of Willard and Gibson,[1] it is desirable to arrange that the end-point in this titration shall be reached under conditions approximating closely to those existing in the solution derived from the chromite sample. Thus, besides using equal amounts of the same indicator, the volume of ferrous ammonium sulphate taken in the standardisation must be equal to that required in the assay, and the conditions of dilution, acid concentration and temperature must be specified for both.

The final conditions have been specified by Hardwick in Part II of this investigation, but taking, for example, 0·5046 g. of potassium dichromate in 400 ml. of 2 *N* sulphuric acid and 25 ml. of phosphoric acid (sp.gr. 1·75), adding 100 ml. of approximately 0·105 *N* ferrous ammonium sulphate, then titrating back the excess with standard decinormal dichromate at 20° C., the relative mean deviation of this method for determining chromate does not exceed 0·04 per cent. when barium diphenylamine sulphonate is used as indicator. The colour change of N-phenyl anthranilic acid is less satisfactory, whilst the oxidation - reduction potentials of ferroin and nitroferroin are too high for use in this titration.

Arsenate does not interfere in this procedure. Vanadium, however, remains quantitatively in the quadrivalent state at the end-point indicated either by barium diphenylamine sulphonate or N-phenyl anthranilic acid, and the interference of vanadate could not be prevented by any variation of this procedure.

Thanks are expressed to Mr. S. H. Bales, Chemical Inspectorate, Ministry of Supply, for encouragement and advice during the prosecution of this work, and to Dr. P. J. Hardwick for a sample of 5-nitro-1 : 10-phenanthroline. Acknowledgment is also made to the Chief Scientist, Ministry of Supply, and to the Government Chemist for permission to publish this work.

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CHEMICAL INSPECTORATE
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The Determination of Chromium in Chromite Part II. Determination of Chromium in a Synthetic Sample of Known Composition

BY P. J. HARDWICK

SYNOPSIS—Four methods in common use for the determination of chromium in chromite were tested on a synthetic mixture of potassium dichromate and "mixed oxides" equivalent in composition to the mineral. All the methods involved fusion with sodium peroxide and removal of most of the excess of peroxide by boiling with water, and the chromate formed was titrated by adding excess of ferrous ammonium sulphate solution and titrating back with dichromate solution. Two of the methods gave satisfactory results (within 1 part in 2000 of the chromium present) after allowance was made for the small amount of vanadium present; they were selected for trial on a standard sample of chrome ore. The other two were more laborious and required amending for accurate work.

FOLLOWING the study of titration methods for the determination of chromate described in Part I,[1] an examination has been made of four methods in common use in this country for determining chromium in chromite. In all four methods the ore is decomposed and chromium oxidised to chromate by fusion with sodium peroxide, usually in a nickel crucible. Most of the excess of peroxide is then destroyed by boiling with water. In three of the four methods the interference of residual peroxide is eliminated by an auxiliary oxidation in acid solution with ammonium persulphate and silver nitrate[2,3] (Method 1) or potassium permanganate in small or large excess[4,5] (Methods 2 and 3, respectively). In the fourth method the alkaline solution of peroxide is boiled for a longer time. The interference of manganese as permanganate or manganese dioxide is eliminated in all cases by boiling with hydrochloric acid (for small amounts of manganese) or by filtration. In the present investigation the chromium as chromate was determined by addition of excess of ferrous ammonium sulphate solution and back-titration with standard potassium dichromate solution, using barium diphenylamine sulphonate as indicator in presence of phosphoric acid. This titration method was chosen for its convenience and for the sharpness of the end-point. Also, provided the ferrous ammonium sulphate solution is standardised against potassium dichromate under the same conditions, particularly with regard to acidity, volume of solution and concentration of dichromate,[6,7] the procedure is capable of yielding exact results. It is necessary, however, to correct for vanadium.

The main object of the investigation was to test the accuracy of these methods, working with a known amount of chromium. For this purpose a synthetic sample was used containing in typical proportions all the principal constituents of chromite, all as oxides or carbonates except chromium, which was present as potassium dichromate. Unnecessary wastage of a standard sample of chromite was thereby avoided. Moreover, it was an advantage to start with all the chromium in the form of a soluble salt, corresponding with complete decomposition of the ore.

The results obtained showed that two of the methods (Methods 1 and 2) were suitable for accurate work. The other two methods required amending.

Experimental

Preparation of a synthetic sample of known composition—

The composition of the mineral chromite varies within wide limits, but as commonly purchased in this country it contains on average about 48 per cent. of chromic oxide. The remainder consists mainly of oxides of iron, aluminium, magnesium and silicon, and may include small amounts of calcium, barium, manganese, titanium, vanadium and nickel.

For the purpose of this investigation a synthetic representative material (subsequently referred to as "mixed oxides") was prepared consisting of an intimate mixture of ignited oxides and carbonates in the following proportion by weight: Fe_2O_3 16; Al_2O_3 15·5; MgO 14; SiO_2 4; $CaCO_3$ 1; MnO_2 0·5; $BaCO_3$, TiO_2, V_2O_5 and Ni_2O_3, each 0·25. Addition of an accurately known weight of $K_2Cr_2O_7$ to a weighed portion of the "mixed oxides" in the ratio 1·79 to 1 provided a sample of known composition containing all the principal constituents of an average chromite in typical proportions with a little K_2O in addition.

Fusion and extraction procedure—

The sample of "mixed oxides" and added potassium dichromate (total weight about 0·7 g.) was fused with 5 g. of sodium peroxide[8] at dull red heat for 5 minutes in a nickel crucible of about 40-ml. capacity. On cooling, the crucible and lid were transferred to a 600-ml. beaker fitted with a cover glass, 100 ml. of water were added and the solution was boiled for 10 minutes to extract the chromate and decompose most of the excess peroxide. The crucible and lid were then rinsed with about 50 ml. of water and removed.

In preliminary experiments the melt was maintained at dull red heat for 15 minutes, but attack of the nickel by the peroxide was severe and crucibles of wall-thickness about 0·7 mm. could not be safely used for more than 2 or 3 fusions. Parallel experiments in which a mixture of sodium peroxide and sodium hydroxide (Theobald's mixture[9]) was used as flux showed reduced attack of the nickel and the crucible served for 6 fusions. In subsequent work with sodium peroxide, however, it was found that the time of fusion could be shortened to 5 minutes for complete decomposition of the sample. Under these conditions about 0·4 g. of nickel was dissolved during a fusion and the average life of a crucible was 5 or 6 fusions. Examination of the crucibles spectrographically showed that the nickel contained only a trace of chromium (less than 0·01 per cent.) and approximately 0·3 per cent. of manganese. No vanadium was detected.

Treatment of the extract by different methods—

Method 1—Auxiliary oxidation with ammonium persulphate and silver nitrate[2,3]—The extract was acidified with 120 ml. of diluted sulphuric acid (1 + 3), warmed to dissolve the precipitate and transferred to a 1000-ml. conical flask. After dilution with water to 500 ml. to decrease the sulphuric acid concentration to about 2 *N*, the auxiliary oxidation was carried out in the usual manner[2] and the small amounts of permanganate and manganese dioxide present were destroyed by boiling with dilute hydrochloric acid. After cooling, a measured volume (100 ml.) of standard ferrous ammonium sulphate solution was added from a pipette and the small excess titrated back with 0·1 *N* potassium dichromate solution after addition of 25 ml. of phosphoric acid (sp.gr. 1·75) and 5 drops of a 0·3 per cent. solution of barium diphenylamine sulphonate in water as indicator. At the end-point the indicator was sensitive to 0·02 ml. of 0·1 *N* potassium dichromate solution added to a total volume of about 600 ml. of solution.

Small departures from standard practice[2] were the higher initial concentration of hydrochloric acid used (20 ml. of diluted hydrochloric acid (1 + 3) per 500 ml. of solution) and the longer time of boiling given (15 minutes) to destroy persistent traces of manganese dioxide and remove chlorine. Separate experiments in which known amounts of potassium dichromate were boiled with hydrochloric acid under similar conditions showed that no reduction of dichromate occurred.

Method 2—Auxiliary oxidation with permanganate in small excess—The extract was acidified and diluted to 500 ml. as in Method 1, and 1 to 2 ml. of approximately 0·1 *N* potassium permanganate were added to the hot solution to give a small excess, shown by the

deepening amber colour. After boiling for 5 minutes, the excess of permanganate was destroyed by boiling with hydrochloric acid and the chromate titrated as in Method 1.

Method 3—Auxiliary oxidation with permanganate in large excess (Vignal Method[4,5])—The extract was acidified and diluted to 500 ml. as in Method 1. It was then heated to boiling and a 5 per cent. solution of potassium permanganate was slowly added until a brown precipitate appeared. Approximately 5 ml. of a 10 per cent. solution of manganous sulphate were added and the solution was boiled for 5 minutes, cooled and filtered by suction through a closely packed pad of asbestos (previously boiled with dilute nitric acid) or through a sintered glass crucible (Jena 3 G4). The precipitate of hydrated manganese dioxide was washed with hot water and the filtrate and washings were diluted to 500 ml. and titrated as in Method 1.

Method 4—Alkaline filtration[8]—The extract was boiled for a further 5 minutes to destroy most of the remaining peroxide and the precipitate of hydroxides allowed to settle. The solution was then filtered through a hardened paper (Whatman No. 52, 12·5 cm.) at room temperature to avoid reduction of the chromate, or through sintered glass, and the precipitate washed 8 to 10 times with 30-ml. quantities of water until the washings were colourless. The combined filtrate and washings were acidified with 120 ml. of diluted sulphuric acid (1 + 3), cooled to room temperature and titrated as in Method 1.

Results

The results obtained for the chromium content of samples containing a known weight of potassium dichromate added to 0·26 g. of "mixed oxides" are summarised in Table I. The weight of potassium dichromate taken was checked by titration against standard ferrous ammonium sulphate solution of an equal amount of dichromate weighed out at the same time as the test sample. In Methods 1 and 2 the chromic oxide found was corrected for a small consistent "blank" with the "mixed oxides" amounting to 0·0004 g. of chromic oxide, which was chemically equivalent to the known amount of vanadium present (0·00125 g. V_2O_5).

Table I

Determination of chromium in a synthetic sample by different methods

Method	Test No.	Potassium dichromate added g.	Equivalent wt. of chromic oxide g.	Chromic oxide found g.	Error g.
1	1	0·4643	0·2399	0·2398	− 0·0001
	2	0·4643	0·2399	0·2398	− 0·0001
	3	0·4643	0·2399	0·2399	0·0000
	4	0·4643	0·2399	0·2399	0·0000
	5	0·4644	0·2400	0·2399	− 0·0001
	6	0·4644	0·2400	0·2399	− 0·0001
	7	0·4643	0·2399	0·2399	0·0000
	8	0·4643	0·2399	0·2400	+ 0·0001
2	1	0·4642	0·2399	0·2399	0·0000
	2	0·4642	0·2399	0·2398	− 0·0001
	3	0·4641	0·2398	0·2399	+ 0·0001
	4	0·4641	0·2398	0·2399	+ 0·0001
3	1	0·4644	0·2400	0·2436	+ 0·0036
	2	0·4644	0·2400	0·2429	+ 0·0029
4	1	0·4642	0·2399	0·2394	− 0·0005
	2	0·4642	0·2399	0·2330	− 0·0069
	3	0·4642	0·2399	0·2353	− 0·0046
	4	0·4642	0·2399	0·2351	− 0·0048

The results, calculated as chromic oxide, show satisfactory agreement with the weights taken in all the tests of Methods 1 and 2. The maximum error is about 1 in 2000 which is admissible in most analytical work. The results obtained by Method 3 are 1 to 2 per cent. too high. "Blanks" with the "mixed oxides" by this method were also high and variable. Separate experiments showed that the error probably arose through peptisation of the hydrated manganese dioxide precipitate; it was reduced by washing the precipitate with a 1 per cent. solution of sulphuric acid instead of water and was completely eliminated[10] when a wash solution containing 5 per cent. of potash alum and 1 per cent. of sulphuric acid was used. Amended in this way the method gave satisfactory results but was more laborious than Methods 1 and 2.

The results obtained by Method 4 are low. The error was found to be due mainly to retention of chromium by the bulky insoluble residue, consisting largely of nickel hydroxide. Separate experiments[10] in which the sample was fused with Theobald's mixture instead of sodium peroxide, to reduce the amount of nickel dissolved from the crucible, showed that the residue still retained a small amount of chromium (about 0·0005 g. of Cr_2O_3) even after repeated washing with hot water. By fusing the ignited residue with the flux, however, as in the method described by Hillebrand and Lundell[2] using sodium peroxide, the chromium was almost completely recovered. The amended method, involving two fusions and extractions followed by an auxiliary oxidation with ammonium persulphate and silver nitrate in acid solution, and removal of traces of permanganate by boiling with hydrochloric acid, gave results comparable in accuracy with those obtained by Methods 1 and 2 but was laborious. Methods 1 and 2 were therefore considered the simplest and most reliable of the methods tested and were selected for further trial with a standard sample of chrome ore.[11]

I am indebted to the Government Chemist and to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

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Department of the Government Chemist
Government Laboratory, W.C.2

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The Determination of Chromium in Chromite
Part III. Determination of Chromium in a Standard Sample of U.S. National Bureau of Standards Chrome Refractory No. 103 by Selected Methods

By F. J. BRYANT and P. J. HARDWICK

Synopsis—The two selected methods, both involving fusion with sodium peroxide, were simple, rapid and capable of giving reproducible results. In the standard sample dried to constant weight at 105° to 110° C. they indicated chromium equivalent to 36·96 and 37·03 per cent. of Cr_2O_3 respectively. The higher results by the second method were attributed to incomplete elimination of chlorine from the decomposition of traces of manganese dioxide on boiling with dilute hydrochloric acid before the chromate titration. When the boiling was prolonged, the second method gave consistent values of 36·97 per cent. Allowing for the presence of 0·08 per cent. of vanadium in the sample the average results by the two methods were 36·92 and 36·93 compared with the certificate figure of 36·97 per cent. of Cr_2O_3.

Introduction—Of the four methods previously tested (Part II[1]) using a synthetic sample containing a known amount of chromium, two (Methods 1 and 2) gave satisfactory results after correction for the small amount of vanadium present and seemed suitable for routine or umpire determinations of chromium in chromite. This Part describes independent analyses of chrome refractory No. 103 of the U.S. National Bureau of Standards by these two methods. In both methods, any vanadium present reacts similarly to chromium, being reduced from V^{V} to V^{IV} on the addition of ferrous ammonium sulphate and not re-oxidised in the back-titration

with potassium dichromate. On the other hand, titration with potassium permanganate causes the re-oxidation of vanadium to V^v but the reaction is slow, and even under the optimum conditions described in Part I[2] there is some sacrifice in the sharpness of the end-point. From information available it seemed that vanadium was unlikely to be present in more than small amounts in most ores. In view of the convenience of the dichromate titration and the satisfactory results obtained with the synthetic sample, it was decided to follow the procedure described in Part II and apply a correction for vanadium determined separately, if necessary, by a colorimetric method.

Experimental

The test sample was a finely ground standard sample of U.S. National Bureau of Standards Chrome Refractory No. 103, previously well mixed (sieving tests showed that all but a very small fraction of the sample passed a 200-mesh B.S. sieve, of aperture 0·0030 inch). Weighed portions of the sample were dried at 105° to 110° C. to constant weight before test. The certificate value of the percentage of chromium in the sample was unknown to the analysts during the work.

The volumetric techniques used by the two independent analysts varied slightly, and are described below.

(1) In one case (F. J. B.) the strength of the ferrous ammonium sulphate solution was so adjusted that when 100 ml. were added to the chromate solution the excess was of the order of 1 to 5 ml., which was determined by adding the standard dichromate solution from a 10-ml. burette. The standard dichromate solution was accordingly made slightly weaker than the ferrous ammonium sulphate solution and the standardisation performed by taking 100 ml. of the iron solution, adding 100 ml. of the dichromate solution and completing the titration from the 10-ml. burette.

The actual concentrations selected, after initial experiments had shown the ore to contain approximately 25 per cent. of chromium, were 0·074 *N* dichromate and 0·075 *N* ferrous ammonium sulphate in 5 per cent. sulphuric acid. Potassium dichromate was taken as the primary standard and one calibrated 100-ml. pipette and one 10-ml. burette were used throughout.

(2) In the other case (P. J. H.) the graduated apparatus was limited to a 50-ml. pipette and a 50-ml. burette, both previously re-calibrated. Ferrous ammonium sulphate solution in 5 per cent. by volume sulphuric acid was freshly standardised against 0·1 *N* potassium dichromate solution both before and after each group of titrations. To minimise burette drainage errors, the ferrous ammonium sulphate solution was made slightly stronger than the dichromate solution and the main bulk of the titrant was added from the pipette. The titration was then completed by the addition of dichromate solution from the burette. Usually, on re-standardising the ferrous ammonium sulphate reagent after a period of about an hour, titrations agreed to within 0·02 ml. in a titration of about 50 ml. of 0·1 *N* dichromate.

All reagents were of AnalaR quality and the potassium dichromate was re-crystallised and dried to constant weight at 105° to 110° C. Spectrographic examination of the crucibles used for sodium peroxide fusions showed that the nickel contained negligible amounts of chromium and vanadium and approximately 0·3 per cent. of manganese. A "blank" with the reagents and a control determination with a known amount of potassium dichromate (added as standard dichromate solution to the alkaline extract of the fused peroxide) were carried out with each group of test determinations.

Methods and results

Method 1—Auxiliary oxidation with ammonium persulphate—

This method, which had given satisfactory results in previous work with the synthetic sample, seemed suitable for routine or umpire determinations of chromium in chromite. It is described in detail here for convenience of reference.

An accurately weighed amount, approximately 0·5 g., of the well mixed, finely ground sample dried to constant weight at 105° to 110° C. was transferred to a nickel crucible of about 40-ml. capacity and was thoroughly mixed with 5 g. of sodium peroxide. A thin layer of peroxide was sprinkled over the surface of the mixture, the crucible was covered with a nickel lid and heated gently over the small flame of a Bunsen burner for about 5 minutes until the contents were molten. Heating was then continued at dull redness for a further

5 minutes with occasional careful swirling of the contents of the crucible to ensure thorough mixing. On cooling, the crucible and lid were transferred to a 600-ml. beaker having a cover glass, 100 ml. of water were added and the solution was boiled for 10 minutes to decompose most of the peroxide. The crucible and lid were then thoroughly rinsed and removed, the alkaline extract was acidified with 120 ml. of diluted sulphuric acid (1 + 3), warmed to dissolve the precipitate, and transferred to a 1000-ml. conical flask. (In the first four tests the slightly turbid solution was filtered at this stage and the small residue ignited and examined for unattacked ore. The residue was found to consist mainly of manganese dioxide with a trace of chromium (0·0001 g. of Cr_2O_3) probably not completely washed from the filter paper). Water was added to increase the volume to 500 ml. and followed by 5 ml. of nitric acid (sp.gr. 1·42), 25 ml. of 1 per cent. silver nitrate solution and 5 g. of ammonium persulphate. After addition of one or two silica chips to prevent bumping, the solution was heated to boiling and boiled vigorously for 15 minutes to destroy excess of persulphate. The solution was cooled slightly, 20 ml. of diluted hydrochloric acid (1 + 3) were added to destroy permanganate and vigorous boiling was continued for a further 15 minutes to expel chlorine. On cooling, a measured volume (100 ml.) of standard ferrous ammonium sulphate solution was added from a pipette and the excess titrated back with potassium dichromate solution after addition of 25 ml. of phosphoric acid (sp.gr. 1·75) and 5 drops of a 0·3 per cent. solution of barium diphenylamine sulphonate in water as indicator.

The results obtained by both analysts are set out in detail in Table I. Tests 1 to 12 were carried out at one laboratory (P. J. H.) and 13 to 20 at the other (F. J. B.). In each group of tests the "blank" was less than 0·00005 g. of Cr_2O_3 (≡ 0·02 ml. of 0·1 *N* $K_2Cr_2O_7$). All weights of Cr_2O_3, in this and subsequent tables, are expressed to the nearest 0·05 mg.

TABLE I

DETERMINATION OF CHROMIUM IN A STANDARD SAMPLE OF CHROME ORE BY METHOD 1

Test No.	Wt. of air-dried sample g.	Loss on drying at 105° to 110° C. g.	Moisture %	Wt. of dried sample taken g.	Wt. of Cr_2O_3 found: in solution g.	Wt. of Cr_2O_3 found: in residue g.	Total wt. of Cr_2O_3 found g.	Cr_2O_3 in dried sample % found
1	0·5238	0·0026	0·50	0·5205	0·19200	0·00010	0·19210	36·91
2	0·5229	0·0026	0·50	0·5197	0·19170	0·00010	0·19180	36·91
3	0·5238	0·0026	0·50	0·5202	0·19260	0·00010	0·19270	37·04
4	0·5213	0·0026	0·50	0·5178	0·19110	0·00010	0·19120	36·93
Control				0·12730	0·12725	0·00010	0·12735	
5	0·5220	0·0025	0·48	0·5190	0·19165		0·19165	36·93
6	0·5243	0·0025	0·48	0·5180	0·19110		0·19110	36·90
Control				0·12730	0·12735		0·12735	
7	0·5232	0·0029	0·55	0·5203	0·19280		0·19280	37·06
8	0·5275	0·0029	0·55	0·5246	0·19390		0·19390	36·96
Control				0·12730	0·12745		0·12745	
9	0·5140	0·0023	0·45	0·5117	0·18935		0·18935	37·00
10	0·5102	0·0023	0·45	0·5079	0·18770		0·18770	36·96
Control				0·12740	0·12740		0·12740	
11	0·5146	0·0025	0·49	0·5121	0·18910		0·18910	36·93
12	0·5104	0·0025	0·49	0·5079	0·18765		0·18765	36·95
Control				0·12740	0·12740		0·12740	
13				0·5000			0·18480	36·96
14				0·5000			0·18500	37·00
15				0·5000			0·18470	36·94
16				0·5000			0·18520	37·04
17				0·5000			0·18475	36·95
18				0·5000			0·18460	36·92
19				0·5000			0·18460	36·92
20				0·5000			0·18485	36·97
Control				0·1875			0·18760	
							Mean ..	36·96

The difference of 0·16 per cent. between the extreme values found for the percentage Cr_2O_3 in the dried sample was greater than expected in view of the consistent results obtained with the synthetic sample by this method and the sharp titration end-point, which was sensitive to within 0·02 ml. of 0·1 *N* potassium dichromate in a total titration volume of

about 75 ml. in tests 1 to 12 and 95 ml. in tests 13 to 20. The control determinations, on the other hand, showed an excellent recovery of chromium in line with the precision of the titrations. The slight excess of chromium found in one instance (Control 7, 8) was probably due to traces of chlorine remaining after decomposition of permanganate (derived from the nickel crucible) with hydrochloric acid although the solution was boiled for 15 minutes before titration and the "blank" was satisfactory.

The variation in the percentage of Cr_2O_3 found in the test samples was probably not due to differences in moisture content as all samples were dried overnight at the same temperature (105° to 110° C.) to constant weight. The percentage moisture found in the sample (0·5 ± 0·05 per cent.) varied slightly in tests made on different days. The average percentage of Cr_2O_3 in the dried sample, corrected for the presence of 0·08 per cent. of vanadium* is 36·92 per cent., which is slightly lower than the certificate value of 36·97 per cent. of Cr_2O_3 for chrome refractory No. 103.

METHOD 2—AUXILIARY OXIDATION WITH PERMANGANATE IN SMALL EXCESS—

Satisfactory results were obtained by this method in previous work (Part II) with the synthetic sample. With the advantages of being somewhat shorter than Method 1 and requiring less expensive reagents, the method was considered more suitable for routine work.

The procedure of fusion with sodium peroxide, subsequent boiling with water and acidification with 120 ml. of diluted sulphuric acid (1 + 3) was the same as in Method 1. After addition of 5 ml. of nitric acid (sp.gr. 1·42) and warming to dissolve the precipitate, the almost clear solution was transferred to a 1000-ml. conical flask and diluted to 500 ml. with water. 1 to 2 ml. of 0·1 *N* potassium permanganate solution were added to give an excess as shown by the deepening amber colour, and the solution was then boiled for 5 minutes. After cooling slightly, 20 ml. of diluted hydrochloric acid (1 + 3) were added and boiling continued for 15 minutes to destroy permanganate or manganese dioxide and remove traces of chlorine. Addition of one or two silica chips helped to maintain even boiling. On cooling, a measured volume (100 ml.) of standard ferrous ammonium sulphate solution was added from a pipette and the excess was titrated back with 0·1 *N* dichromate solution as described in Method 1. The results obtained are shown in Table II.

TABLE II

DETERMINATION OF CHROMIUM IN A STANDARD SAMPLE OF CHROME ORE BY METHOD 2

Test No.	Wt. of air-dried sample g.	Loss on drying at 105° to 110° C. g.	Moisture %	Wt. of dried sample taken g.	Wt. of Cr_2O_3 found g.	Cr_2O_3 in dried sample % found
21	0·5251	0·0029	0·55	0·5222	0·19335	37·02
22	0·5229	0·0026	0·50	0·5203	0·19265	37·03
Blank					nil	
Control				0·12730	0·12745	
23	0·5094	0·0025	0·49	0·5069	0·18780	37·05
24	0·5138	0·0025	0·49	0·5113	0·18945	37·05
Blank					0·00030	
Control				0·12740	0·12775	
25	0·5163	0·0025	0·48	0·5138	0·19020	37·01
26	0·5086	0·0025	0·49	0·5061	0·18735	37·02
Blank					nil	
Control				0·12740	0·12755	
					Mean ..	37·03

The results obtained by this method are more consistent than those obtained by Method 1 and the maximum difference of 0·04 per cent. of Cr_2O_3 is of the order expected from the precision of the titration. The mean percentage of Cr_2O_3 in the sample, however, is 0·07 higher than the average of the twenty determinations by Method 1. Allowing for 0·08 per cent. of vanadium in the sample, the corrected figure of 36·99 per cent. of Cr_2O_3 is in close agreement with the certificate value of 36·97 per cent.

A slight excess of chromium was found in control determinations by this method and in one instance (Blank 23, 24) a small "blank" was recorded. These discrepancies were probably due to traces of chlorine remaining in the solution after boiling with dilute hydrochloric acid to destroy permanganate and suggested that the percentage of Cr_2O_3 found in the test samples

* 1 ml. of 0·1 *N* $K_2Cr_2O_7 \equiv$ 0·0051 g. of V $\equiv$ 0·00253 g. of Cr_2O_3.

was slightly greater than the true value. The presence of chlorine in the final solution after 15 minutes' boiling may have been due to the slow reaction of hydrochloric acid with the traces of manganese dioxide remaining after treatment of the boiled alkaline solution with dilute sulphuric acid. In Method 1, oxidation with ammonium persulphate and silver nitrate in the presence of nitric acid converted all the manganese to permanganate, giving a clear solution, especially noticeable with the "blank." No difficulty was then experienced in removing traces of chlorine by boiling for 15 minutes with dilute hydrochloric acid in blank or control determinations except in one instance (Control 7, 8). In the present method it appeared necessary to boil for at least 15 minutes after complete reduction of permanganate and the disappearance of the last traces of turbidity due to manganese dioxide.

This was confirmed by the results of the following series of tests (Table III) in which, after addition of dilute hydrochloric acid, boiling was continued for 5 to 10 minutes until the solutions were quite clear and then for a further 15 minutes to expel traces of chlorine. Tests 27 to 30 were carried out at one laboratory (P. J. H.) and 31 to 34 at the other (F. J. B.). It is seen that satisfactory results were obtained in the control determinations, having regard to the limits of experimental error set by the sensitivity of the titration end-point (0·02 ml. of 0·1 *N* $K_2Cr_2O_7 \equiv 0{\cdot}00005$ g. of Cr_2O_3).

Consistent results were obtained for the percentage of Cr_2O_3 in the test sample but, as expected, the average was slightly lower than that previously found. After correcting for 0·08 per cent. of vanadium, the average percentage of Cr_2O_3 was 36·93, which agrees with 36·92 per cent. found by Method 1 and compares reasonably well with the certificate value of 36·97 per cent.

TABLE III

DETERMINATION OF CHROMIUM IN A STANDARD SAMPLE OF CHROME ORE BY MODIFIED METHOD 2

Test No.	Wt. of air-dried sample g.	Loss on drying at 105° to 110° C. g.	Moisture %	Wt. of dried sample taken g.	Wt. of Cr_2O_3 found g.	Cr_2O_3 in dried sample % found
27	0·5031	0·0024	0·48	0·5007	0·18500	36·95
28	0·5022	0·0023	0·46	0·4999	0·18485	36·98
Blank					0·00005	
Control				0·12730	0·12740	
29	0·5054	0·0024	0·48	0·5030	0·18585	36·95
30	0·5041	0·0023	0·46	0·5018	0·18555	36·98
Blank					nil	
Control				0·12730	0·12735	
31				0·5000	0·18475	36·95
32				0·5000	0·18510	37·02
33				0·5000	0·18495	36·99
34				0·5000	0·18485	36·97
Blank					0·00020	
Control				0·1875	0·18750	
					Mean ..	36·97

Acknowledgment is made by one of us (F. J. B.) to Mr. E. Booth for experimental assistance.

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Extraction and Photometric Estimation of Some Metals with 8-Hydroxyquinoline

By C. H. R. GENTRY and L. G. SHERRINGTON

Synopsis—The pH conditions for the complete extraction of certain metals from aqueous solutions by means of a 1 per cent. solution of 8-hydroxyquinoline in chloroform are reported. Metals investigated include aluminium, copper, ferric iron, manganese, molybdenum, nickel and stannic tin. For the photometric estimation of traces of stannic tin, extraction with 8-hydroxyquinoline is put forward as a valuable addition to known methods. As a further example of the application of the results, brief mention is made of the separation of iron, nickel, cobalt, copper and manganese from very pure molybdenum trioxide. It is shown that the extraction of 8-hydroxyquinolinates of the heavy metals is a useful method of purifying solutions of many reagents used in trace analysis.

The solubility in chloroform of the 8-hydroxyquinolinates of many metals can be of analytical importance in three respects:

(*a*) as a means of separation of trace impurities prior to their determination by other methods,

(*b*) as providing a medium for photometric or fluorimetric analysis, since the chloroform solutions are strongly coloured and some show a marked fluorescence,

and (*c*) for the purification of reagents by extraction of the metallic impurities.

The first systematic publication on the extraction of metals with a chloroform solution of 8-hydroxyquinoline, by Moeller,[1] described the use of a 0·01 *M* reagent solution with four extractions for each determination. Under these conditions the pH ranges for complete extraction were very narrow for some of the metals. By using a 1 per cent. (about 0·07 *M*) reagent solution, the extraction of aluminium was made effectively complete in one operation over a wide pH range.[2] The same conditions have been adopted by Westwood and Mayer[3] for the determination of cerium in cast iron. Lacroix,[4] who investigated the properties of the oxinates of aluminium, gallium and indium, used a 0·1 *M* solution of reagent (about 1·45 per cent.). The work of this author is of special interest for the valuable theoretical treatment given.

In the present work the 1 per cent. reagent concentration has been retained and the other conditions of extraction also follow those previously used for the extraction of aluminium, with the exception of a shorter time of shaking. The primary object of the investigation has been the establishment of the pH range for complete extraction of the several metals. As is to be expected, the results differ widely from those found by Moeller. Of special significance in the present work is the new method of photometric analysis offered by the extraction of stannic tin. In view of the paucity of good methods for the estimation of traces of tin, special attention has been given to this finding.

Experimental

For each element a series of experiments was made at various pH values, extracting in each test 50 ml. of the aqueous solution, containing a fixed amount (50 or 200 μg.) of the element, with 10 ml. of a 1 per cent. solution of 8-hydroxyquinoline in chloroform. After shaking for 1 minute, the chloroform layer was run off into a small flask containing about 1 g. of anhydrous sodium sulphate. A blank determination was made, omitting the element under investigation. AnalaR reagents were used where available. The acid buffer solutions were made from sodium acetate solution to which either hydrochloric or acetic acid was added, and the alkaline buffer solutions were prepared from mixtures of sodium hydroxide and bicarbonate. In the determination of some of the metals 10 ml. of 10 per cent. sodium potassium tartrate was included in the buffer solution. In order to keep the blank value at a low level it was found necessary to purify the solutions of sodium acetate, sodium bicarbonate and sodium potassium tartrate by the method to be described later.

The absorption of the chloroform solution was measured on the Spekker absorptiometer, using the mercury vapour lamp and a 1-cm. cell. The filter combination used was Ilford 601

with Chance No. 8 (O.V.1), excepting for iron, for which Wratten 50 and Chance O.B.2 were used. The choice of filters was in accordance with the transmission curves reported by Moeller. In the determinations, the pH of the aqueous solution was measured with the glass electrode immediately after the separation of the chloroform layer.

Results

(*a*) Aluminium—

The pH conditions for the extraction of aluminium in the absence of tartrate, which interferes, have been described previously.[2] For the sake of completeness the graphical representation of the results is included in Fig. 1.

Replacement of the Wratten No. 2 filter, previously used, by the Ilford 601 filter, together with the Chance No. 8 filter gave a linear calibration curve. The deviation from linearity previously reported was due to the transmission of some red radiation by the filter pair then used.

(*b*) Copper—

The results obtained with copper in the presence of tartrate are shown in Fig. 1. It can be seen that complete extraction of copper occurs in the pH range 2·8 to 14. Throughout this work the term "complete extraction" is used where at least 98 per cent. of the metal present has been extracted in one operation, as shown either by a second extraction or by comparison of the drum reading with results at other pH values.

(*c*) Iron—

Ferric iron in the presence of tartrate can be completely extracted in the pH range 2·5 to 12·5 (Fig. 1). With a double or triple extraction the iron could be completely extracted from even more acid solution, say at pH 2, a fact of value in the separation of iron from other heavy metals.

(*d*) Manganese—

On attempting the extraction of bivalent manganese in the presence of tartrate, it was found that, although extraction occurred in the alkaline range, the Spekker readings showed small but significant variations at slightly differing pH values. It was thought that these variations might be due to partial atmospheric oxidation of the manganese. Two series of experiments were therefore made, the first in presence of 5 ml. of 5 per cent. sodium sulphite solutions and the second in presence of 1 mg. of potassium ferricyanide. Under the latter oxidising conditions, complete extraction and constancy of drum readings were found in the pH range 7·2 to about 12·5. These conditions are therefore recommended for the photometric determination of manganese; but for the separation of manganese, the ferricyanide may be omitted.

(*e*) Molybdenum—

The colour of the molybdenum hydroxyquinolinate extract was not so intense as for the other metals, and it was necessary to use 200 μg. of molybdenum in each experiment. Tartrate interfered with the extraction, but in its absence molybdenum could be completely extracted in the pH range 1·6 to 5·6.

(*f*) Nickel—

The complete extraction of nickel in the presence of tartrate was possible in the pH range 4·5 to 9·5 (Fig. 1).,

(*g*) Tin—

It was found that stannic tin could be extracted from an acid solution, pH 2·5 to 5·5, to give a yellow chloroform layer. The transmission curve of the chloroform solution is shown in Fig. 2, from which the broad minimum at 3850 A. can be seen. This decided the choice of filters: Chance No. 8 and Ilford 601 transmitting the mercury 4078 and 4047 A. lines.

By the treatment of a series of solutions containing different amounts of tin, all at pH 3·5, a calibration curve was obtained. This was linear over the range examined, *i.e.*, up to 280 μg., corresponding to a drum difference reading of 0·70. A 2-minute shaking period was used, and the extraction was made promptly after adjusting the pH of the solution,

as otherwise somewhat lower results were obtained. The presence of tartrate seriously interfered with the extraction of tin, but in the presence of 0·4 g. of ammonium oxalate 95 per cent. of the 200 μg. of tin present could be extracted in the pH range 5 to 6.

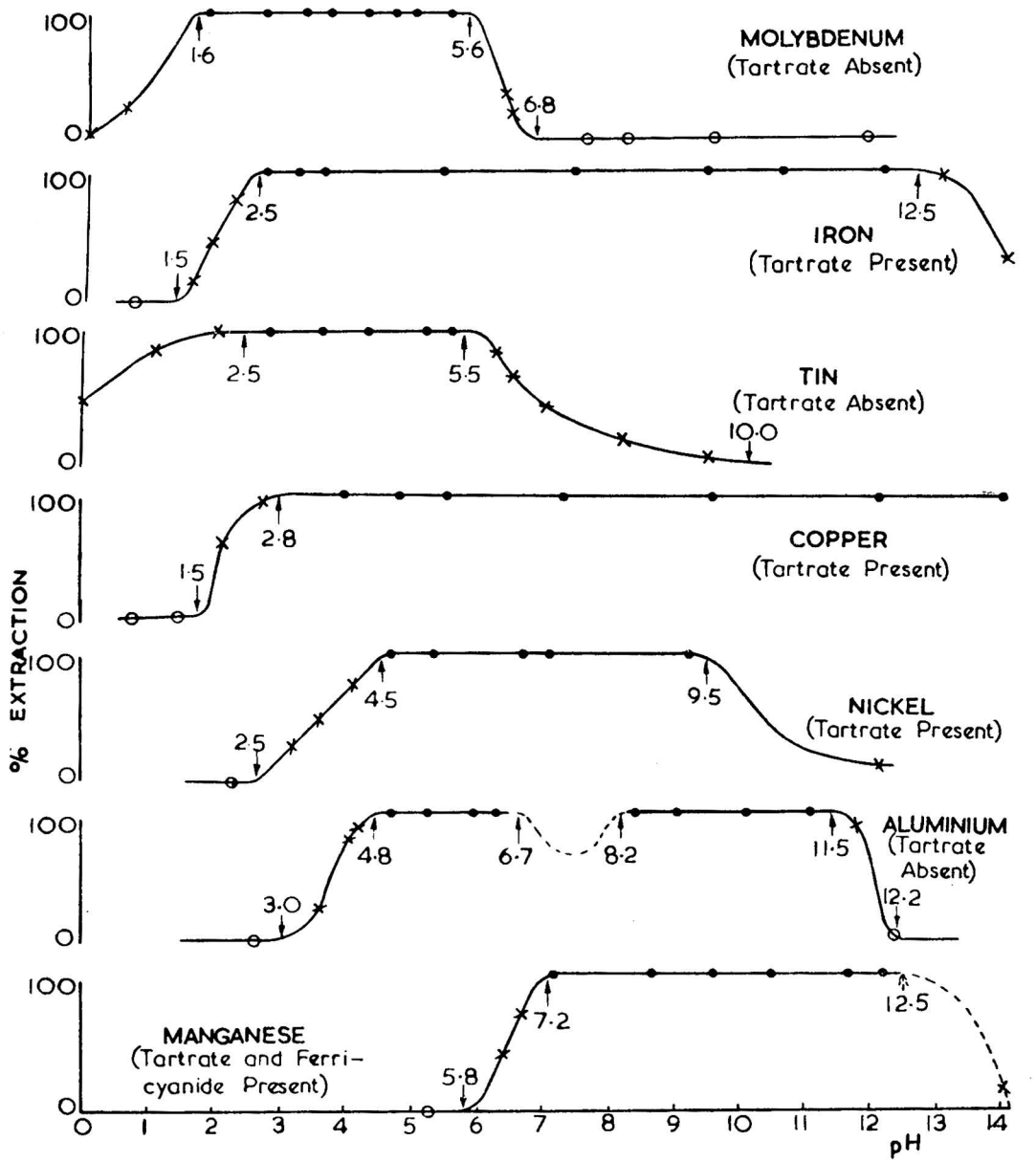

Fig. 1. Effect of pH on extraction
O = No extraction
× = Part extraction
● = Complete extraction

(*h*) OTHER METALS—

Attempts to obtain conditions for the complete extraction of bismuth in one operation were unsuccessful, although partial extraction was possible in the pH range 5 to 12. Even in the absence of all tartrate and chloride, and using a bismuth sulphate solution and acetate buffers, the absorptiometer readings showed marked changes with pH.

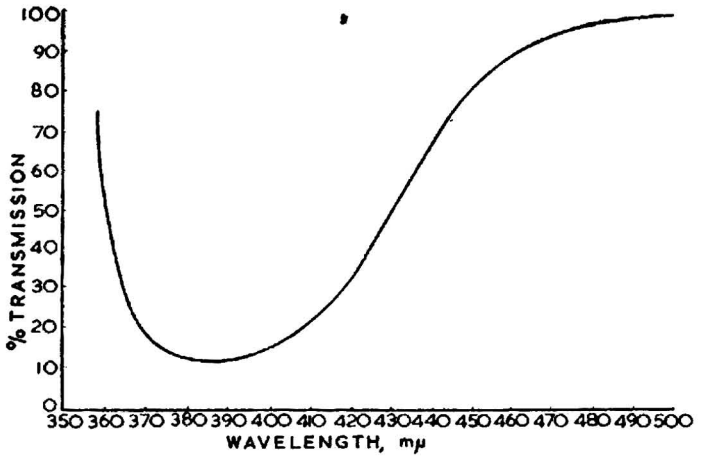

Fig. 2. Transmission curve for tin 8-hydroxyquinolinate

Cobalt, like manganese, gave peculiar results, thought to be due to oxidation by air in alkaline solution. Complete extraction of cobalt was possible in a pH range of about 5·7 to 9·5, but the drum readings showed variations larger than the expected experimental errors. Attempts to obtain constant readings under either oxidising or reducing conditions, as used for manganese, were not successful.

In view of the analytical association of arsenic, antimony and tin, the extraction of the first two elements was investigated under the conditions used for tin. Arsenic did not interfere but antimony could be extracted from acetate solutions to some extent over the range for the complete extraction of tin. Tartrate partially suppressed the extraction of antimony, whilst the presence of oxalate prevented extraction from solutions with a pH greater than 5·0.

Discussion

As was to be expected, with the present conditions, the pH ranges for complete extraction differ markedly from those reported by Moeller.[1]

Where possible, tartrate has been added to the aqueous solution, to prevent precipitation of the hydrous oxides, which would otherwise occur. The presence of these hydrous oxides would considerably increase the extraction time necessary for the complete formation of the 8-hydroxyquinolinates. Molybdenum, tin and aluminium, however, cannot be extracted completely in the presence of tartrate. It is nevertheless possible to remove all but a negligible amount of aluminium in the presence of tartrate from a solution at pH 9·5 by using a triple extraction. Whether tartrate is added in a particular application will depend on the conditions required.

An example of the application of this method as a means of separating trace impurities is the determination of iron, nickel, cobalt, copper and manganese in very pure molybdenum trioxide. By double extraction with a chloroform solution of 8-hydroxyquinoline at pH 9 in the presence of tartrate the impurities from 5 g. of sample are separated from the molybdenum and concentrated into 10 ml. of chloroform solution. It is then a comparatively simple matter to determine the impurities by standard photometric methods on a micro-scale. It is possible by this means to determine the above-mentioned impurities in amounts down to 0·00002 per cent. in the molybdenum trioxide.

For the direct photometric determination of most of the elements investigated, chloroform extraction of the 8-hydroxyquinolinate has no advantages over other available methods, particularly in view of its non-selective nature. An exception to this is the determination of aluminium by the masking of interfering elements, a procedure described in a previous paper. A further exception is the photometric determination of tin, which is not easily determined in trace amounts by known methods. The application of the 8-hydroxyquinoline method is dependent on the ready separation of tin from other elements by distillation of the chloride or bromide. An accurate photometric estimation of tin in the distillate can then be made by the procedure previously described. Conditions of distillation must be

carefully controlled to prevent the interference of antimony, but otherwise the method is specific among common elements.

This new method for the determination of tin has been applied to samples of tungsten and tantalum compounds with a considerable saving in time over the methods previously used.

A third general application of the extraction of the 8-hydroxyquinolinates is found in the removal of heavy-metal impurities from analytical reagents. This method is generally applicable to soluble salts of ammonium, the alkali metals or the alkaline earths, provided that the pH of the solution falls within the desired range, preferably from 4·5 to 9·5, as can be seen by inspection of Fig. 1. The procedure adopted is to shake the solution of the salt with a 1 per cent. solution of 8-hydroxyquinoline in chloroform, run off the chloroform layer, and repeat the process until the organic layer is colourless. Excess of 8-hydroxyquinoline can be removed from the aqueous solution by several extractions with chloroform. Finally, the chloroform dissolved in the solution can be removed by bubbling air through the solution. Experiments have shown that this procedure will reduce the heavy metal content of solutions to a very low level and the method is very suitable for the preparation of chemicals used in trace analysis.

Conclusions

The work reported in this paper was originally undertaken as part of an investigation of analytical methods for the refractory metals, but the results are felt to be of more general interest. As a means of separation of trace impurities and as a method of reagent purification, chloroform extraction of 8-hydroxyquinolinates should have many applications. For the estimation of traces of tin, the direct photometric method using 8-hydroxyquinoline would seem to have some advantages over other methods and it should repay study.

We wish to thank Mr. J. A. M. van Moll and the Directors of Philips Electrical Limited, for permission to publish this paper.

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Material Research Laboratories
Philips Electrical Ltd.
Mitcham Junction, Surrey

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A Method for the Dry Assay of Sulphides and Oxides of Lead and Bismuth

By J. A. SMYTHE

Synopsis—A rapid test tube method of dry assay of lead in galena is based on the observation that if a solution of galena in molten caustic potash is heated with stannous sulphide the lead is quantitatively reduced to metal and may be obtained as a button. The method is applicable also to the oxides of lead. Bismuth in its oxide or sulphide may be similarly assayed. The action of the stannous chloride is discussed: heated alone with molten caustic potash it is entirely oxidised to the stannic state with evolution of hydrogen.

Pellets of caustic potash melt at 170° C. If galena is present, it begins to dissolve at once in the molten alkali and there is formed, with mineral of high grade, a clear solution, coloured more or less red according to whether the galena contains much or little iron. The solution contains lead oxide and potassium sulphide and addition of water to it reverses the reaction, the black sulphide being precipitated.

When caustic potash and stannous sulphide are slowly heated together the alkali, as soon as it is melted, attacks the stannous sulphide and hydrogen is liberated, increasing in quantity as the temperature rises and producing at 180° to 190° C. vigorous effervescence. The melt is clear and yields a clear solution with water. On acidification, hydrated stannic oxide, with perhaps some stannic sulphide, is precipitated. No stannous compound is formed in this reaction.

In presence of galena the reaction between the alkali and stannous sulphide is modified, in so far as the yield of hydrogen is greatly reduced; at the same time metallic lead is separated quantitatively. This reaction is suggested here as the basis of a method for the assay of galena and it has also been found capable of extension to the oxides of lead and to the sulphide and oxide of bismuth.

METHOD—

The operation is carried out in a test tube and the composition of the charge found most suitable, having regard to accuracy of result, ease of manipulation and economy of time is: PbS 0·35 g., SnS 0·70 g. and KOH 4·0 g. The galena, crushed to pass a 60- or 80-mesh sieve, is shot into the test tube down a chute of glazed paper and the potash pellets are added and melted in a small flame, a roll of filter paper being placed in the tube to absorb moisture. When the galena has dissolved, or nearly so, the paper is removed and the charge of stannous sulphide added in 5 or 6 portions through a small funnel; the heating and swirling of the tube are so regulated that the froth, caused by the escape of hydrogen, does not rise more than about an inch up the tube, and particles of stannous sulphide, borne upwards on the froth, subside into the liquid. The lead soon separates as a spongy mass and the heating is increased gently until the melting-point of lead (327° C.) is reached. The metal then appears as a brilliant bead in a translucent liquid and the reaction is complete. After solidification the melt is dissolved in water, the muddy liquid decanted and the bead cleaned with a little dilute hydrochloric acid, dried on filter paper and weighed. The whole operation can be done in 5 to 10 minutes. If the tube should spring a small leak after the lead has separated, but before complete melting, the sponge can be extracted, pressed between filter papers and heated with a small amount of potash, and the metal recovered without loss. It may be mentioned that it seems necessary, in order to get accurate results, that the galena should be dissolved, or nearly so, in the potash before the addition of the reducing agent. Early experiments in which the two were ground finely together gave results almost invariably 1 or 2 per cent. low.

The method has been tested on three samples of galena: (*a*) a selected cleavage cube without visible impurity, (*b*) a high-grade concentrate from Sipton, Northumberland, and (*c*) a low-grade concentrate from Halkyn, Flintshire, containing much dirty gangue and blende. The dry assay by the ordinary crucible method was done on (*b*) and (*c*), and the determination of lead by wet methods on all three. The results, as percentages of lead, are given below. Those by the new method are from three consecutive trials and the means of these.

Sample	Crucible assay %	Wet assay %	New method, %	
				Mean
(*a*)	—	85·0	85·1, 85·3, 84·6	85·0
(*b*)	79·8	82·8	83·0, 83·3, 82·3	82·9
(*c*)	57·5	61·3	61·2, 61·2, 60·9	61·1

Some experiments have been made on the effect of adding to the charge sulphides, commonly associated with galena, that are easily reducible and yield metals soluble in lead at a relatively low temperature. These were added in such quantity as would give, on complete reduction and absorption by the lead, an alloy containing 3 per cent. of the metal. The effect of addition of orpiment was not reflected in the quantitative results and the bead was malleable and contained little more than a trace of arsenic. With stibnite somewhat more antimony was found in the bead, but its weight was not seriously affected. It is probable that these sulphides form sulpho-salts not easily reduced. With bismuth sulphide, however, there was complete reduction to bismuth, which was taken up by the lead.

Application to oxides of lead—Peroxide of lead is "balled up" by the potash and appears to be but slightly soluble in it, but this does not affect its reducibility. The two other oxides are fairly soluble. The method used is the same as for galena, but it is advantageous to

increase the quantity of stannous sulphide to 1 g. and that of potash to 5 g. The experimental results, given below as percentage of lead, show good agreement with those from the wet assay.

	Wet assay %	New method %
PbO	89·8	90·0, 90·1
Pb_3O_4	89·4	89·6, 89·8
PbO_2	85·6	85·3, 85·0

Application to sulphide and oxide of bismuth—The reaction with these compounds goes rather more easily than with the compounds of lead, being facilitated by the low melting-point of the metal (268° C.). The charge is as for galena. Some results, as percentages of bismuth, are given below.

	Wet assay %	New method %
Bi_2S_3	77·5	77·7, 77·6, 77·4
Bi_2O_3	89·5	89·0, 89·2, 89·2

The experimental results cited above attest the value of this reaction as a quantitative one. The obvious advantages lie in the economy of material and fuel and the great saving in time. Duplicate determinations of galena, for example, can be completed in 30 to 40 minutes, including the weighings, and the requisite skill for rapid and successful operation is easily acquired. Perhaps the only drawback with galena is that the silver cannot be determined in the bead. Metallic tin brings about the same reaction as stannous sulphide, but it cannot be used in its place, first because of slow reaction, and secondly because some tin is dissolved by the precipitated lead and protected thereby from reaction with the potash. A bead obtained in this way was found to contain 20 per cent. of tin.

NOTE ON STANNOUS SULPHIDE—

The material bought as stannous sulphide and used in these experiments is uniform, black, lustrous and well crystallised; it contains but little impurity. It is, however, not pure stannous sulphide, but a mixture, obviously a solid solution, of stannous and stannic sulphides. The analytical figures are: Sn (total) 74·4, S 24·5 (98·9), Sn (stannous) 57·3 per cent. From these the proximate composition is calculated as: SnS 73·5 and SnS_2 26·5 per cent., or perhaps more accurately as: SnS 51·6 and Sn_2S_3 48·4 per cent. For the sake of simplicity the trade name stannous sulphide* has been used in the foregoing account, but it is desirable in what follows to distinguish it from pure stannous sulphide and it may be conveniently, if loosely, termed "tin sulphide." Experiments on the liberation of hydrogen from tin sulphide and potash are informative and throw some light on the reactions involved in the method of assay. The volume of hydrogen equivalent to 1 g. of tin is calculated as 188 ml. at N.T.P. One gram of tin sulphide contains 0·573 g. of stannous tin and should therefore yield 107·7 ml. of hydrogen. The volume actually observed was 107·5 ml., in excellent agreement with this. In presence of added PbS (the two ground together finely) the volume of hydrogen was greatly reduced, being 64·7 ml. from a 2 : 1 mixture and 19 ml. from a 1 : 1 mixture. If the mixing were of the intimacy inherent in a solid solution, then further diminution in the yield of hydrogen would be expected. A suitable solid solution for testing this was made by heating together lead and tin sulphide. The preparation contained a small amount of Pb - Sn alloy and its proximate composition was: PbS 48·9, SnS 45·6, Pb 4·3 and Sn 1·2 per cent.; total Pb 46·7 per cent., total Sn 37·1 per cent. This material with molten potash gave 23·5 ml. of hydrogen per g. and 45·1 per cent. of Pb. Calculating from the hydrogen value, the amount of SnS destroyed by the alkali and hence the residue available for reduction can be found. This is equivalent to 47·1 per cent. of PbS, and would thus yield 40·8 per cent. of Pb. Adding the free lead to this gives the total reduced lead as 45·1 per cent., which is identical with the observed value.

When the same solid solution was ground with its own weight of PbS and melted with alkali, not a trace of hydrogen was evolved and the yield of lead was 69·0 per cent. The whole of the tin was there employed in the reduction, the lead equivalent of which is 64·8. Adding to this the free lead gives the total yield as 69·1 per cent., a figure almost identical

* This reagent was supplied by The British Drug Houses Limited, who will guarantee supplies to contain not less stannous sulphide than that used in these experiments.

with the observed value. These results have been substantiated by similar tests with another solid solution, richer in tin and poorer in lead, the details of which may be omitted.

It is evident that the reducing action of stannous sulphide in these reactions is not brought about by hydrogen, but that the active agent is stannous oxide. This, in molten alkali, is oxidised by water; but when oxides of lead and bismuth are present, these act directly as oxidising agents. There is a further possibility that in some cases the stannous oxide suffers self-oxidation and reduction, yielding stannic oxide and tin and that the latter plays the part of the reducing agent. With tin sulphide, the presumed constituent of the sesqui-sulphide is resolved into stannous and stannic sulphides and the latter, being converted directly into stannic oxide, has no influence on the reduction process.

NOTE ON BEHAVIOUR OF MOLYBDENUM SULPHIDE—

Since the work described above was carried out, I have examined the reaction between MoS_2 and caustic potash. The molybdenum sulphide was prepared from molybdenite and contained 56·4 per cent. of molybdenum, equivalent to 94 per cent. of MoS_2. This yielded when melted with potash 127 ml. of hydrogen per gram, that is 135 ml. for the pure sulphide. This is close to the calculated yield of 139 ml., based on the assumption that MoS_2 is converted into MoO, which is then oxidised by water, as is SnO.

When MoS_2 is fed into the melt of PbS and KOH, lead separates as a sponge in a sludge greatly thickened with molybdenum compounds. It seems impossible to melt this lead owing to the excessive frothing that takes place towards the end of the reaction. The sponge can, however, be recovered and melted into a bead with a little fresh caustic potash, but the yield is low, of the order 80 per cent. The reaction is therefore useless for quantitative work.

It may be mentioned that FeS_2 does not yield hydrogen with caustic potash, nor is it capable of reducing PbS in the alkali melt.

KING'S COLLEGE
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The Determination of Small Quantities of Copper in Lead and Lead Alloys

BY P. L. WILLMOTT AND F. J. RAYMOND

SYNOPSIS—The method is based on the formation of the copper complex with sodium diethyldithiocarbamate in strongly ammoniacal solution, its extraction therefrom by ether and photometric reading of the ether extract. A 5-g. sample is dissolved in nitric acid and evaporated and, after addition of sulphuric acid, the major part of the tin, antimony and lead is filtered off. Interference by nickel and cobalt are avoided by addition of dimethylglyoxime to the neutralised filtrate and filtration. For complex formation the filtrate is treated with ammonia, ammonium citrate and the reagent. The ether extract is read in a Spekker absorptiometer. Bismuth interferes, producing a similar but much feebler colour. A correction for it is made by carrying out a similar determination in which the formation of the copper complex is prevented by prior addition of cyanide. Copper contents up to 0·01 per cent. are determinable to within 0·00005 per cent. By suitable choice of sample weights and dilutions the method may be adapted to copper contents up to 10 per cent.

DURING the past year there has been an increasing demand for chemical lead and also lead pipe made to B.S. 1085. In order to meet the heavy demand, it was essential that the works refining processes were not delayed, and that results of chemical tests on the partially refined metal were reported as quickly as possible.

For determining small quantities of copper there were two methods available. The method given by the British Standards Institution is a very lengthy process, and not suitable for routine works control. An alternative method is to electrolyse the copper from solution, so that it may be redissolved in a small volume and determined colorimetrically with ammonia.

This method is also very lengthy, since it requires taking large quantities of the sample because of the rather insensitive colour reaction.

Among the most sensitive reagents for copper is sodium diethyldithiocarbamate. A brown precipitate of the very slightly soluble copper carbamate is formed when an aqueous solution of sodium diethyldithiocarbamate is added to a very slightly acid, neutral or alkaline (ammoniacal) solution of a cupric salt. In very dilute solutions a colloidal suspension is formed which is suitable for colour comparison. Gum arabic, gum acacia, gum tragacanth or gelatin may be used as protective colloid to prevent the coagulation of the precipitate.

The copper carbamate complex is soluble in a number of organic solvents, such as amyl alcohol, amyl acetate, bromo-benzene, chloroform or ethyl ether. The resulting brown solution may be used for the colorimetric determination of copper, either by comparison with standards similarly prepared or by measuring its light absorption.

With many of the heavy metals sodium diethyldithiocarbamate forms precipitates, most of which are soluble to a greater or less extent in the organic solvents named. Zinc, cadmium, mercuric mercury, silver, lead and tin salts give white precipitates, whilst ferric iron yields a brown-black precipitate in neutral or acid solutions. However, in alkaline citrate solutions there is no reaction if the pH is maintained above 9. Bismuth yields a similar colour to that given by copper, although the colour produced is only about one-thirtieth to one-fiftieth as intense.

Of the metals that interfere with the copper determination, nickel, cobalt and bismuth are the worst offenders. Zinc, cadmium, mercuric mercury, silver, lead and tin salts cause no interference after extraction because their solutions have 100 per cent. transmittancy. Iron is not likely to be found in large quantities in lead. The interference from nickel and cobalt is avoided by adding 1 ml. of 0·5 per cent. dimethyl glyoxime solution to the alkaline solution. The nickel is precipitated and removed by centrifuging or filtering. The cobalt remains in the aqueous layer as an orange complex, which is not extracted with ether.

The interference from bismuth is best overcome by a difference method. Copper diethyldithiocarbamate is destroyed by dilute solutions of potassium cyanide, whilst the bismuth compound is not affected. Strong solutions of potassium cyanide, however, make the extraction of the bismuth complex difficult, and may cause bismuth to revert to the aqueous phase if an ethereal solution of the complex is shaken with very concentrated potassium cyanide solution. Investigation by the authors has shown that less potassium cyanide is required to prevent the formation of the copper complex than is required to destroy the complex once it has been formed.

Solutions of copper diethyldithiocarbamate in ether are very stable and undergo no change in intensity over a period of many months if kept in stoppered bottles to prevent evaporation of the ether.

The procedure described is very accurate and detects as little as 1 μg. of copper. The total time taken in a determination is about 20 minutes, made up as follows: preparation of the sample, 1 min.; weighing the sample, 1 min.; solution of sample, 4 min.; precipitation and cooling, 4 min.; filtering, 5 min.; extraction and comparing colour, 5 min.

In order to check the accuracy of the method, a solution of pure lead nitrate was prepared and different amounts of pure copper nitrate were added. The following table shows the results obtained.

Copper added, % on amount of lead present	Copper found, % on amount of lead present
0·00005	0·00005
0·00010	0·00010
0·00015	0·00015
0·00050	0·00050
0·00100	0·00095
0·00350	0·00355
0·00440	0·00440
0·01000	0·01000
0·03000	0·03050

The synthetic samples contained lead nitrate equivalent to 5 g. of lead. A further series of tests was performed on synthetic samples containing different amounts of bismuth, and in every test the result found was within 0·00005 per cent. of the true figure when calculated on the amount of lead present.

Method

Solutions required—

(1) Sulphuric acid, 50 per cent. v/v.

(2) Ammonium citrate solution. Dissolve 250 g. of citric acid in 250 ml. of water. Cool and add 250 ml. of aqueous ammonia, sp.gr. 0·880.

(3) Potassium cyanide solution in water, 0·5 g. per 100 ml.

(4) Sodium diethyldithiocarbamate solution in water, 0·5 g. per 100 ml.

Procedure—

Weigh two separate 5-g. portions of the sample and place each in a 300-ml. tall-form beaker. Dissolve each in 15 ml. of water and 7 ml. of nitric acid, sp.gr. 1·42. The sample will dissolve rapidly if in the form of thin rollings. When it has dissolved, boil down to small volume and then take up in the minimum quantity of water. This treatment will eliminate the bulk of the tin and antimony from solution. Add 10 ml. of 50 per cent. sulphuric acid and cool thoroughly. Filter off the lead sulphate through a fairly fine paper; a Whatman No. 530 is recommended. Wash well with cold water until free from acid.

Neutralise the filtrate with ammonia, using litmus as indicator. (If the presence of nickel or cobalt be suspected, add also 1 ml. of ammoniacal 0·5 per cent. dimethylglyoxime solution. Allow to stand 5 minutes and then filter through a Whatman No. 530 paper. In absence of nickel and cobalt this treatment can be omitted.)

To one of the two test solutions add a 10-ml. excess of aqueous ammonia (sp.gr. 0·880), 10 ml. of ammonium citrate solution (Reagent 2) and 10 ml. of sodium diethyldithiocarbamate solution (Reagent 4). Cool and transfer to a 200-ml. separating funnel. Rinse out the beaker with 25 ml. of ether and add the rinsings to the solution in the funnel. Shake vigorously under running water for about 1 minute and allow the two layers to separate. (The lower, aqueous, layer should be colourless, and should remain so when a few ml. of the sodium diethyldithiocarbamate solution are added.)

Collect the coloured ethereal layer in a 100-ml. graduated measuring flask. Rinse out the funnel with ether saturated with reagents and add the rinsings to the main solution in the flask. Dilute to the 100-ml. mark with ether saturated with reagents.

Shake to mix the extract and determine the transmittancy as a Drum Reading 1, on the Spekker absorptiometer, with a water-to-ether setting of 1·00. For copper contents below 0·003 per cent. (calculated on sample) use an Ilford violet filter No. 601 and the large 4-cm. cells. For copper contents between 0·002 and 0·010 per cent. use the 1-cm. cells and the same filter. The 1-cm. cells with an Ilford blue-green filter No. 603 should be used for copper contents between 0·01 and 0·03 per cent.

The Drum Reading 1 is a measure of copper plus bismuth, and in order to obtain the true copper figure a difference method is employed.

To the other test, which has been left standing after the filtrate has been neutralised with ammonia as described above, add 1 ml. of 0·5 per cent. potassium cyanide (Reagent 3) for each 0·01 per cent. or part of 0·01 per cent. of copper plus bismuth found from the first uncorrected test. Add a 10-ml. excess of aqueous ammonia (sp.gr. 0·880), 10 ml. of the ammonium citrate solution and 10 ml. of the sodium diethyldithiocarbamate and continue as before. Determine the transmittancy as Drum Reading 2. This is due to bismuth alone.

The drum difference due to copper is equal to Drum Reading 1 minus Drum Reading 2. Standard graphs are prepared from pure standard copper nitrate solution and drum differences plotted against per cent. of copper (on 5 g. sample).

Abbreviated method—

For routine testing the test may be modified. Weigh only one sample of 5 g. and proceed as in the method given above to determine copper plus bismuth. Determine the transmittancy as Drum Reading 1. Pour the ethereal solution back into the separating funnel and add about 30 ml. of water and 5 ml. of 0·5 per cent. potassium cyanide solution. Shake for 1 minute. Allow the two layers to separate and discard the aqueous layer. Determine the transmittancy of the ethereal layer as Drum Reading 2. The difference in drum reading is that due to copper, and the percentage may be read off the appropriate graph.

NOTES—

When the solution is neutralised with ammonia a precipitate may form. This is due to antimony and is caused by insufficient boiling down. The precipitate should be filtered off through a Whatman No. 541 paper.

The quantities of the ammonia, citrate and carbamate prescribed should be adhered to. Excess of sodium diethyldithiocarbamate causes a white precipitate to form which does not dissolve in the ether. It does not effect the test except by making separation of the two layers difficult.

If very small quantities of copper are present, an initial weight of 10 g. should be taken and the extract made up to only 25 ml. In this case, if the graphs used are based on 5-g. samples, the result must be divided by 8.

High copper contents can be determined by the above procedure if smaller weights of sample are taken. For a 10 per cent. copper - lead master alloy it is recommended that 0·5 g. be taken and dissolved, the lead precipitated and filtered off, and the filtrate made up to 500 ml. and 10 ml. (equivalent to 0·01 g. of sample) taken for the determination.

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136 SIBLEY GROVE
MANOR PARK
LONDON, E.12

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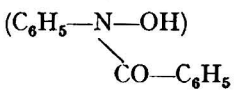
Gravimetric Determination of Copper, Iron, Aluminium and Titanium with N-Benzoylphenylhydroxylamine

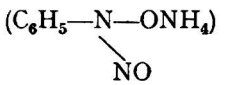
BY SUDHIR CHANDRA SHOME*

SYNOPSIS—N-benzoylphenylhydroxylamine, which can be easily prepared, and preserved indefinitely, has been used successfully for the gravimetric determination of copper, iron, aluminium and titanium. Copper, iron and aluminium can be determined by weighing the precipitate directly and the presence of appreciable amounts of other metals like beryllium, cobalt, cadmium, manganese, nickel, uranium (sexivalent) and zinc does not interfere with the procedure. The precipitation of iron is interfered with by the presence of aluminium and chromium. It is possible to determine copper in presence of phosphoric acid, but the separation of iron and aluminium from phosphoric acid is not possible. In the determination of titanium with benzoylphenylhydroxylamine, the precipitate should be ignited to oxide before weighing. Titanium has been separated from aluminium but iron and phosphoric acid interfere with the precipitation of the metal.

IN an attempt to improve upon certain defects of cupferron, the ammonium salt of N-nitrosophenylhydroxylamine, as an analytical reagent, a series of allied organic compounds were examined by the author.[1] It was observed that N-benzoylphenylhydroxylamine



unlike cupferron (free acid)



possessed the following useful properties: (i) the compound was stable towards heat, light and air and could be preserved indefinitely, (ii) it was soluble in hot water, (iii) the precipitates

* Present address, Corrosion Section, Department of Metallurgy, Cambridge University.

formed with metal ions became granular on heating and (iv) the precipitates were not contaminated with the organic reagent when formed in hot solution and therefore were directly weighable. The object of the present investigation was to study the use of this new organic reagent in the determination of copper, iron, aluminium and titanium.

Experimental

Preparation and properties of benzoylphenylhydroxylamine—

Benzoylphenylhydroxylamine was prepared by a slight modification of the method of Bamberger.[2] Phenylhydroxylamine (30 g.) was dissolved in warm water (1200 ml.) and the solution was filtered. The filtrate was cooled, a little sodium hydrogen carbonate was added and benzoyl chloride (45 g.) was then added drop by drop while the phenylhydroxylamine solution was stirred vigorously. About 30 g. of sodium hydrogen carbonate were added in small quantities at a time to keep the mixture faintly alkaline. The stirring was continued for 90 minutes and the resulting solid (a mixture of monobenzoyl- and dibenzoyl-phenylhydroxylamine) was filtered and washed with water. The solid was then triturated with 10 per cent. sodium hydrogen carbonate solution in a porcelain mortar for half an hour, filtered and washed with water. By this treatment the entrapped drops of benzoyl chloride were removed. The monobenzoyl derivative was separated from the dibenzoyl derivative by treating the white mixture with aqueous ammonia (sp.gr. 0·88), in which only the monobenzoyl compound dissolved. The solution was filtered and the filtrate was added to a slight excess of dilute sulphuric acid cooled with ice and salt. The monobenzoylphenylhydroxylamine that separated out was then filtered and further purified by recrystallisation from alcohol.

Benzoylphenylhydroxylamine is very slightly soluble in cold water but soluble in hot water to the extent of about 0·5 per cent.; it is soluble in alcohol, benzene, ether, acetic acid and aqueous ammonia solution. The compound is stable towards heat, light and air. It is very weakly acidic in character and no ammonium salt is formed when gaseous ammonia is passed through its solution in ether. Its melting-point is 121° to 122° C.

Reactions with the metal ions—

Bamberger[2] reported that benzoylphenylhydroxylamine gave a green precipitate with copper, and a red coloration with iron salt solutions. He did not study the reactions of the compound with the other metal ions. In the present investigation it was observed that benzoylphenylhydroxylamine formed precipitates with the following ions in weakly acidic or weakly alkaline medium: $Pd^{\cdot\cdot}$, $Pt^{\cdot\cdot\cdot\cdot}$, $Zr^{\cdot\cdot\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Hg^{\cdot}$, $Ag^{\cdot}$, $UO_2^{\cdot\cdot}$, $Ce^{\cdot\cdot\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Ti^{\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, VO_3', WO_4'' and MoO_4''.

Copper, iron and aluminium ions were precipitated separately from hot aqueous solution by adding an alcoholic solution of the organic reagent in slight excess. The precipitates were thoroughly washed with hot water and dried at 110° C. Analysis of these pure complexes indicated that their compositions were as follows: $Cu(C_{13}H_{10}O_2N)_2$, $Fe(C_{13}H_{10}O_2N)_3$ and $Al(C_{13}H_{10}O_2N)_3$. The copper, iron and aluminium complexes were green, red and white and their melting- (also decomposition-) points were 198° to 199° C., 187° to 188° C. and 238° to 239° C. respectively. The complexes were decomposed by moderately concentrated mineral acids. The yellow titanium complex was prepared from the cold solution and purified from excess of reagent by crystallisation from alcohol. Analysis of the titanium complex showed that it was not of any definite composition. The titanium complex was decomposed in presence of considerable amounts of mineral acids. All these metallic complexes were soluble in organic solvents. Copper and iron complexes were slightly soluble in 50 per cent. alcohol, whilst those of aluminium and titanium were more soluble.

Reagents used in the determination of the metals—

(1) *Metals to be determined*—Standard solutions of copper sulphate, ferric alum, potash alum and titanium sulphate were prepared separately by the usual methods. A standard solution of copper chloride was used when copper was to be determined in presence of lead and mercury.

(2) *Foreign ions*—In the study of the effect of different ions on the precipitation of the metals to be determined, alkali salts were used for the solutions of the anions, and chlorides, nitrates and sulphates were used for the solutions of the cations.

(3) *Benzoylphenylhydroxylamine solution*—An alcoholic solution of the organic reagent was used for the precipitation of the metal ions.

pH Adjustment—The pH of the solutions was usually adjusted by adding requisite quantities of 10 per cent. solution of sodium acetate and 1·08 *N* sulphuric acid. Glacial acetic acid was used instead of sulphuric acid when copper was determined in presence of lead and mercury. In the determination of titanium, the standard solution was first neutralised with 6 *N* ammonia solution and then acidified with the necessary amounts of concentrated hydrochloric acid (*d.* 1·15).

All the chemicals used were of A.R. quality.

Determination of copper, iron and aluminium

Procedure—

Take a known quantity of copper, iron or aluminium solution containing about 0·025 g. of copper, 0·015 g. of iron or 0·01 g. of aluminium and add 5 ml. of 1·08 *N* sulphuric acid solution (in the determination of iron in ferric alum, the addition of this acid is not necessary when the ferric alum solution contains the same amount of sulphuric acid). Dilute the solution with distilled water to about 400 ml. and heat to boiling. Dissolve benzoylphenylhydroxylamine (one and three-quarter times the theoretical quantity) in alcohol (15 to 20 ml.), warm the solution and add to the hot solution of the metal. Add 10 ml. of 10 per cent. sodium acetate solution to raise the pH of the solution to about 4·0. Occasionally stir the precipitate formed and heat it on the boiling water-bath for 1 to 2 hours (1 hour for copper precipitate and 2 hours for iron and aluminium precipitates). Filter the precipitate on a No. 4 sintered glass crucible and keep the filtrate for subsequent pH measurement by means of a glass electrode. Wash the precipitate thoroughly with hot water and dry it at 110° C. to constant weight. Calculate the metal content on the basis that the precipitate contains 13·03 per cent. of copper, 8·064 per cent. of iron or 4·064 per cent. of aluminium.

Notes—(*a*) Iron and aluminium precipitates tend to form hard lumps when precipitated above 70° C. and hence the precipitation is carried out at about 65° C. There should be good stirring when the flocculent precipitate is changed to the granular form by heating on the water-bath.

(*b*) During the precipitation of the metals, the benzoylphenylhydroxylamine solution is not allowed to fall on the sides of the beaker, otherwise the organic reagent would be deposited on the sides owing to the evaporation of alcohol and necessitate the use of a large volume of wash-water.

(*c*) In the precipitation of aluminium, the alcohol in the final volume of solution should be not more than 5 per cent., because the aluminium complex is moderately soluble in alcohol.

(*d*) The aluminium complex is very slightly soluble in hot water at 90° C. but is insoluble in boiling water containing a small amount of reagent. The aluminium precipitate is washed with warm water at about 45° C.

Results—

The results of determinations of copper, iron and aluminium are shown in Table I. They indicate that these metals can be determined by weighing their complexes directly.

Effect of pH on the precipitation of copper, iron and aluminium—

The precipitation of copper, iron and aluminium was quantitative between the pH values of 3·6 to 6·0, 3·0 to 5·5 and 3·6 to 6·4 respectively. The metals were not precipitated completely when the pH of the solution was lower than these ranges and at higher pH values slightly high results were obtained.

Effect of foreign ions on the precipitation of copper, iron and aluminium—

(*a*) *The presence of anions*—Copper was determined in presence of phosphoric, arsenic and arsenious acids by means of benzoylphenylhydroxylamine. A small amount (5 ml. of 10 per cent. solution) of Rochelle salt was added to the copper solution in order to prevent precipitation of copper phosphate, copper arsenate or copper arsenite when the pH of the solution was raised to about 4·6 by adding sodium acetate solution. The results are given in Table II.

Attempts to separate iron and aluminium from phosphoric acid with the help of benzoylphenylhydroxylamine were not successful. Copper, iron and aluminium were determined separately in presence of large amounts of tartrate ion. Benzoylphenylhydroxylamine gave precipitates with vanadate, molybdate and tungstate ions in acid medium and therefore copper, iron and aluminium could not be separated from these ions.

TABLE I

DETERMINATION OF COPPER, IRON AND ALUMINIUM WITH BENZOYLPHENYLHYDROXYLAMINE

pH of the solution = 3·9 to 4·0

Metal taken g.	Wt. of ppt. g.	Metal found g.	Error g.
0·03156 (Cu)	0·2426	0·03161	+0·00005
0·02777 "	0·2136	0·02783	+0·00006
0·02651 "	0·2037	0·02655	+0·00004
0·02525 "	0·1935	0·02522	−0·00003
0·01728 (Fe)	0·2148	0·01732	+0·00004
0·01656 "	0·2045	0·01649	−0·00007
0·01590 "	0·1964	0·01584	−0·00006
0·01440 "	0·1780	0·01435	−0·00005
0·01021 (Al)	0·2506	0·01018	−0·00003
0·00899 "	0·2220	0·00902	+0·00003
0·00817 "	0·2014	0·00818	+0·00001
0·00817 "	0·1999	0·00812	−0·00005

(*b*) *The presence of cations*—Preliminary experiments revealed that cobalt, cadmium, lead, mercury^{II}, manganese, nickel, uranium^{VI}, and zinc did not form any precipitate with benzoylphenylhydroxylamine at pH 4·0. Copper, iron and aluminium were, therefore,

TABLE II

DETERMINATION OF COPPER IN PRESENCE OF PHOSPHORIC, ARSENIC AND ARSENIOUS ACIDS

pH of the solution = 4·5 to 4·7

Copper taken g.	Acid added g.	Wt. of ppt. g.	Copper found g.	Error g.
0·02525	0·16 (P_2O_5)	0·1930	0·02515	−0·00010
"	0·02 "	0·1938	0·02525	0·00000
"	0·10 (As_2O_5)	0·1942	0·02530	+0·00005
"	0·10 (As_2O_3)	0·1943	0·02531	+0·00006

determinable in presence of the above-mentioned ions. Results are recorded in Table III, and show that copper, iron and aluminium can be separated from many other different metal ions.

Benzoylphenylhydroxylamine precipitated tin, titanium and zirconium ions in acid solution. Copper, iron and aluminium could not be determined in presence of each other or in presence of any of the three above-mentioned ions by means of this organic reagent. The precipitation of iron with benzoylphenylhydroxylamine was interfered with by the presence of chromic ion.

DETERMINATION OF TITANIUM

PROCEDURE—

Take a known quantity of the titanium sulphate solution containing about 0·1 g. of TiO_2 and add distilled water to make the volume about 400 ml. Neutralise the solution with ammonia solution and add 5 ml. of concentrated hydrochloric acid. Precipitate titanium by adding slowly a 10 per cent. alcoholic solution of benzoylphenylhydroxylamine (about double the theoretical quantity) to the clear solution of the metal, with constant stirring. Allow the precipitate to stand for 45 minutes with occasional stirring, filter and wash with dilute hydrochloric acid containing the organic reagent (to prepare the wash-solution, add 10 ml. of benzoylphenylhydroxylamine solution to 1 litre of warm distilled water, cool and mix with 3 ml. of concentrated hydrochloric acid). Ignite the precipitate carefully in a platinum crucible to constant weight and weigh as titanium dioxide.

Notes—(*a*) A gummy substance is formed when titanium is precipitated from a warm solution and hence the titanium solution is kept below 25° C. for precipitation.

TABLE III

DETERMINATION OF COPPER, IRON AND ALUMINIUM IN PRESENCE OF FOREIGN METAL IONS

pH of the solution = 3·9 to 4·1

Metal taken g.	Foreign metal added g.	Wt. of ppt. g.	Metal found g.	Error g.
0·02967 (Cu)	0·08 (Pb)	0·2280	0·02970	+0·00003
" "	" (Hg)	0·2271	0·02959	−0·00008
0·02525 "	0·01 (Be)	0·1939	0·02526	+0·00001
" "	0·12 (Co)	0·1930	0·02515	−0·00010
" "	0·16 (Cd)	0·1939	0·02526	+0·00001
" "	0·08 (Zn)	0·1944	0·02533	+0·00008
0·03156 "	0·06 (Mn)	0·2427	0·03161	+0·00005
" "	0·12 (Ni)	0·2434	0·03171	+0·00015
" "	0·16 (U)	0·2421	0·03154	−0·00002
0·01440 (Fe)	0·14 (Co)	0·1791	0·01444	+0·00004
" "	0·17 (Ni)	0·1784	0·01438	−0·00002
" "	0·28 (Mn)	0·1783	0·01437	−0·00003
" "	0·24 (U)	0·1779	0·01434	−0·00006
" "	0·12 (Zn)	0·1793	0·01445	+0·00005
0·00817 (Al)	0·02 (Be)	0·2008	0·00816	−0·00001
" "	" (Co)	0·2000	0·00813	−0·00004
" "	" (Ni)	0·1999	0·00812	−0·00005
" "	" (Mn)	0·2018	0·00820	+0·00003
" "	" (U)	0·2000	0·00813	−0·00004
" "	" (Zn)	0·2004	0·00814	−0·00003

(*b*) The titanium precipitate is moderately soluble in alcohol and therefore the alcohol in the final solution should not be more than 5 per cent.

RESULTS—

The results of the determination of titanium are shown in Table IV. It was found that this determination was possible when concentrated hydrochloric acid up to 20 ml. was added; the precipitation of titanium was incomplete if more acid was used.

TABLE IV

DETERMINATION OF TITANIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Titanium dioxide taken g.	Titanium dioxide found g.	Error g.
0·1082	0·1081	−0·0001
0·0773	0·0771	−0·0002
0·0742	0·0744	+0·0002
0·0618	0·0616	−0·0002
0·0464	0·0460	−0·0004

EFFECT OF FOREIGN IONS—

Results of determinations of titanium in presence of aluminium ion are recorded in Table V. It is seen that titanium can be determined in presence of aluminium. The metal was determined in presence of large amounts of tartrate ion. The separation of titanium from iron or phosphate ion was not possible.

TABLE V

DETERMINATION OF TITANIUM IN THE PRESENCE OF ALUMINIUM

Titanium dioxide taken g.	Aluminium sesquioxide added g.	Titanium dioxide found g.	Error g.
0·1082	0·10	0·1084	+0·0002
0·1082	0·05	0·1079	−0·0003
0·0773	0·10	0·0770	−0·0003
0·0433	0·05	0·0432	−0·0001
0·0402	0·10	0·0400	−0·0002

Discussion

The essential difference between benzoylphenylhydroxylamine and cupferron is that there is a benzoyl group in the molecule of the former instead of the nitroso group of the latter. Owing to this difference benzoylphenylhydroxylamine has some properties (*e.g.*, stability and solubility in water) better than those of the free acid of cupferron. In the determination of copper, iron and aluminium with this new organic reagent, the precipitate can be weighed directly, which is a distinct advantage over the cupferron method in which the precipitate should be ignited to oxide before weighing. Small quantities of the metals can be determined more accurately with benzoylphenylhydroxylamine since the weight of the metal complex produced from a given amount of metal is nine to thirteen times greater than the weight of the corresponding oxide. Some of the metal ions such as lead and mercury, which interfere with the determination of copper by the cupferron method, have no influence when benzoylphenylhydroxylamine is employed. The results obtained by this new method are accurate. Moreover the organic reagent can be prepared easily and preserved indefinitely.

The acidity of benzoylphenylhydroxylamine is less than that of nitrosophenylhydroxylamine (free acid of cupferron) and therefore, its complexes with the metal ions are more easily decomposed by mineral acids. Owing to this defect, iron cannot be precipitated in strong acid solution and the separation of the metal from aluminium, chromium or phosphoric acid, is not possible. In such circumstances and in the separation of titanium from phosphoric acid, the use of cupferron is preferred.

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Department of Chemistry
Indian Institute of Science
Bangalore, India

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Application of Radio-Frequencies to Conductimetric Analysis (Rectified Radio-Frequency Method)

By G. G. BLAKE

Synopsis—Small changes in the conductivity of solutions, *e.g.*, those associated with neutralisation, as in conductimetric titration, can with advantage be measured by means of radio-frequency oscillations. A recent form of apparatus is described, in which the liquid under test is drawn up into a conductimetric tube around which are three sleeve electrodes; after traversing the liquid in the tube the oscillatory current is rectified and measured with a micro-ammeter. All complications and disturbances due to contact of electrodes with the liquid are avoided. Examples of titration curves are illustrated.

The difficulties encountered in the use of a "conductivity cell" in conductimetric analysis are mainly due to the electrodes being submerged in the solution. By operating at a radio-frequency and employing a "conductimetric tube" fitted with external electrodes[1,2,3] in place of a cell, all such difficulties are avoided and the time and trouble involved in wetting platinised electrodes are eliminated. Colloidal solutions can be used, and precipitation is no longer a serious trouble.

By this new method any amount of solution, down to a quantity as small as one millilitre, can be analysed. The method is suitable therefore both for general and for micro titration.

As a result of investigations carried out since the rectified radio-frequency method was published originally,[1] the author has acquired a considerable amount of further information, which is described in the present paper.

Before giving details of the apparatus used for rectified radio-frequency analysis the new method may be outlined as follows.

A radio-frequency current is applied to an electrode attached to the outside of a glass tube into which successive samples of solution are introduced. The radio-frequency current passes through the sample, emerges via a second external electrode and passes thence through a small rectifier. The rectified current from this is measured by means of a micro-ammeter or a galvanometer.

Given constant frequency and a circuit having fixed values of capacitance and inductance, the micro-ammeter deflections will be proportional to the radio-frequency resistance of the circuit and as the column of solution is the only variable, the deflections will give a direct indication of the radio-frequency resistance of the solution.

(1) RADIO-FREQUENCY OSCILLATOR—

Any type of stable radio-frequency oscillator can be employed, the choice of frequency not being at all critical; 2000 Kc/s. is a suitable value. When making this selection it should be borne in mind that the higher the frequency the greater will be the difficulties experienced through stray capacity, and the lower the frequency the larger will be the dimensions of the inductance, etc.

Two suitable types of oscillator have already been described[1]. For the present application a zero-shunted micro-ammeter in the plate current feed of the oscillator is not required.

(2) THE CONDUCTIMETRIC TUBE AND ITS ACCESSORIES—

Fig. 1 is a diagram embodying the latest developments.

The conductimetric tube—The tube, G, is of thin-walled Pyrex glass 3 mm. in diameter. It has a reservoir at its head connected by rubber tubing to a pipette, P. The original conductimetric tube[1,2,3] was fitted with two external electrodes.

The new tube as seen in Fig. 1 has three external sheath electrodes. These may be of lead or tin-foil wrapped round the tube. By spreading the electric field in this way a smaller screening tube, T, can be employed.

The pipette—In lieu of the glass syringe originally employed, now that the apparatus is smaller, a pipette, P, is used to draw successive samples of solution into the tube. As seen in Fig. 1 this is fitted with an air-inlet valve, V. In the side of the pipette there is a small hole covered by a rubber sleeve stretched over a roller. When in the position shown in the figure the air-inlet hole is closed. Air is admitted by a rotation of the roller which lifts the sleeve when in the proximity of the air-inlet hole. Use of this valve enables air to be bubbled forcibly through the solution after each addition of the reagent.

The micro-burette—On the left-hand side of Fig. 1 there is a micro-burette at the head of which is a length of rubber tube, R, closed by a stopper, K. The burette is filled with the reagent by compressing and then releasing R by means of a clamp, L. The measured units of reagent are delivered as desired by gradually tightening the clamp by means of the thumb-screw, L.

The Rectifier—After passing through the solution, the radio-frequency current is led to a small rectifier, Re (either a "Westector" or a "fixed crystal"). The rectified current, as modified by the radio-frequency resistance of the solution under test, passes through a radio-frequency choke, H, and its value is read by a zero-shunted micro-ammeter.

Another new development is the employment of a very small pre-set condenser, W (Fig. 1); this is seen better in the enlarged drawing at the left-hand bottom corner of the figure. Its object is to by-pass a very small amount of the radio-frequency current directly through the rectifier to ensure that the latter will operate on the straight portion of its characteristic curve. It was found that a perfect shielding of the rectifier was liable to cause distortion of the graphs. When once this "pre-set" condenser has been properly set it should never require any further adjustment. A small hole in the side of the earthed metal screening cylinder, T, is provided through which a screw-driver may be inserted to make the needful adjustment. It should be noted that the conductimetric tube G, choke H and the rectifier Re are all screened and the screening is earthed (see T and T').

The zero-shunt circuit[4]—The zero-shunt may be operated from a 6-volt direct current supply or by rectified alternating current[3] and is used to adjust the zero reading of the micro-ammeter either before or, if necessary, during a titration.

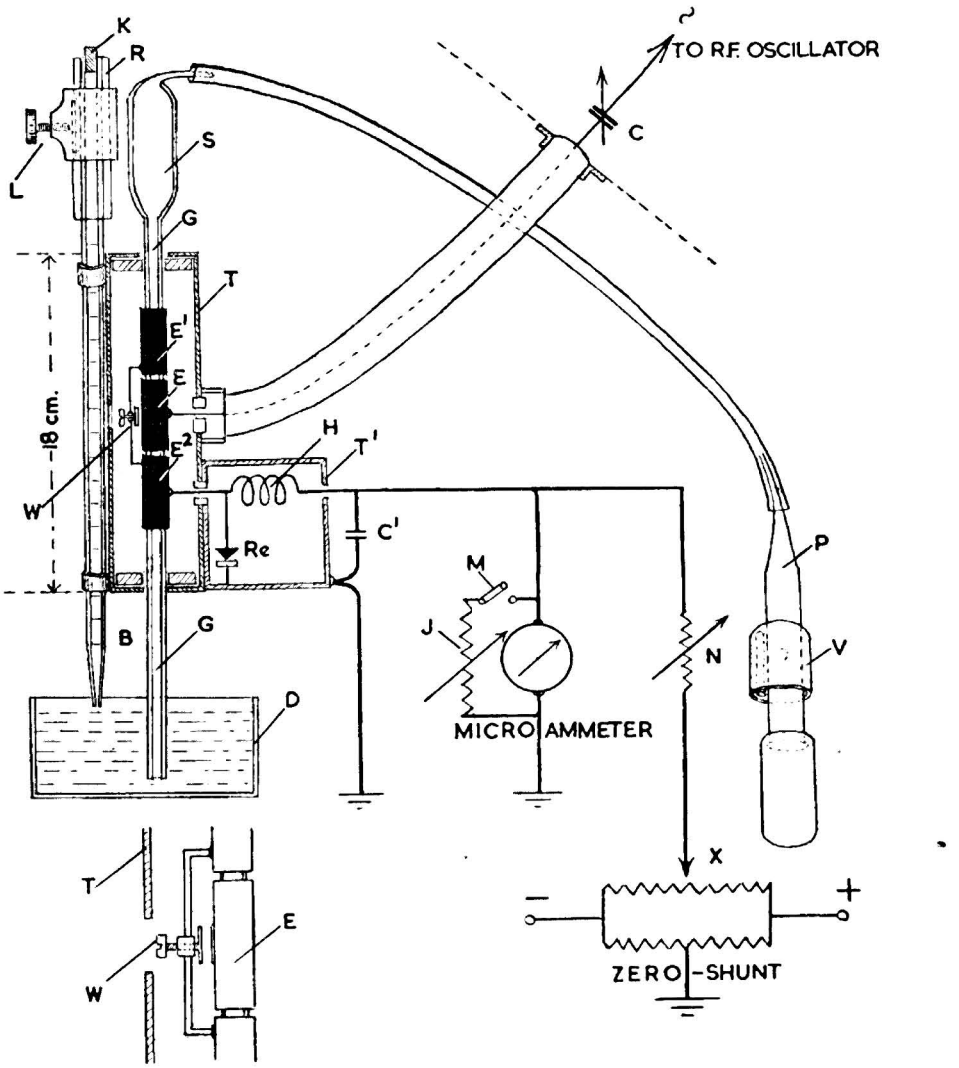
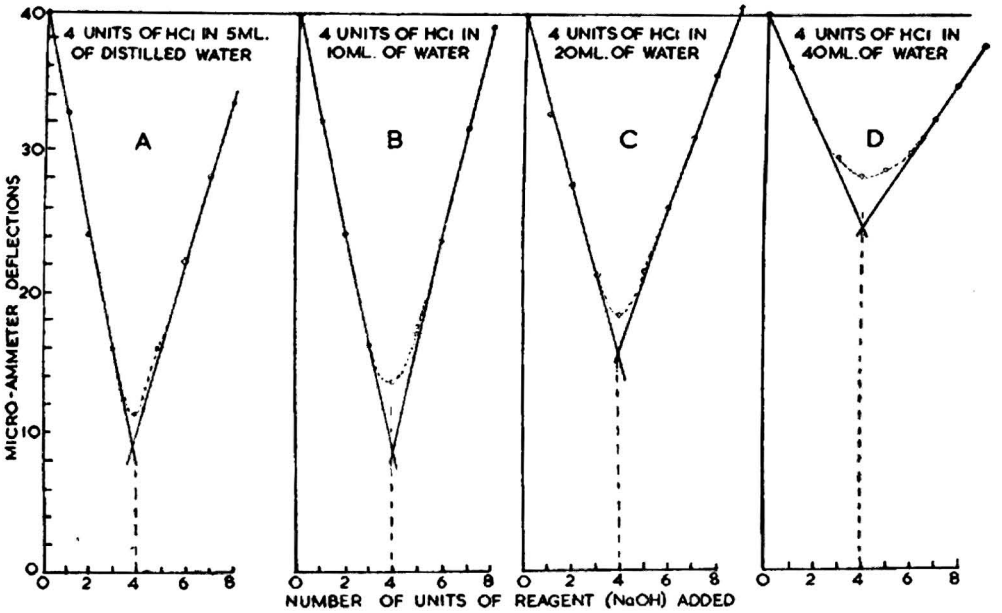


Fig. 1. Conductimetric tube and accessories. This diagram shows several new features, including by-pass condenser, three electrodes (instead of two), micro-burette attached to the screening cylinder and a pipette with an air-inlet valve

It has been shown in the previous papers to which reference has been made that adjustment of the zero-shunt enables any desired point on the scale of the micro-ammeter to be used as zero, whether or not the instrument has a scale with zero at its centre, also that if during a titration it becomes obvious that the subsequent deflections will out-distance the scale in either direction the needle can then be set forward or backward, as the case may require, by any desired amount, and so long as the amount of this readjustment is deducted from (or added to) all the successive readings the titration can then proceed.

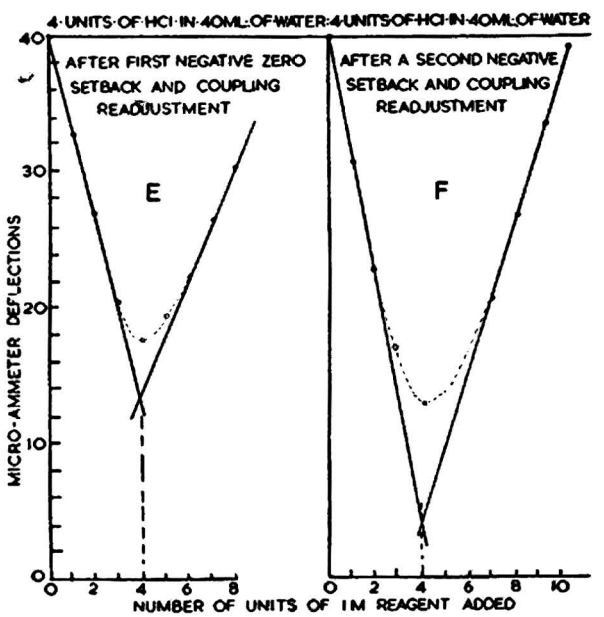
Coupling condenser—The coupling condenser, C, which should have as good a zero as possible, is of great importance. It regulates the radio-frequency current applied to the conductimetric tube. It is used in the following manner.

First it is set at zero. Let us suppose that the scale of the particular micro-ammeter to



Normal meter zero for all graphs and coupling readjustment to 40μa. 1 unit = 5 microlitres. The concentrations of both the HCl and the NaOH were 1 *M*

Fig. 2. The four graphs in this figure, plotted under the conditions described in the text, show how the form of the graphs acquire a more obtuse angle as the concentration of the acid solutions is reduced



1 unit = 5 microlitres of 1 *M* solution

Fig. 3. The two graphs in this figure are for the same low concentration as that for graph D of Fig. 2, and show how the form of the latter is improved: first after one negative zero set-back, and still more after a second negative zero set-back

be employed reads from 0 to 60 μa. The conductimetric tube having been filled with a sample of the solution under analysis, the coupling condenser, C, is adjusted until a certain pre-selected deflection, say 40 μa., is obtained. This adjustment of the coupling is maintained throughout the entire analysis, 40 μa. being taken as the starting-point of the graph. This was so for each of the graphs in Fig. 2.

Some applications

Figs. 2 and 3 are a series of titration graphs made with the apparatus illustrated in Fig. 1. The end-point is determined by extending the two straight portions of the graph to the point of intersection.

The four graphs shown in Fig. 2 illustrate the effect of reducing the concentration of the solution. It will be noted that although the correct value of the end-point is obtained in all the tests, the sensitivity of the method is reduced as the solution concentration is reduced.

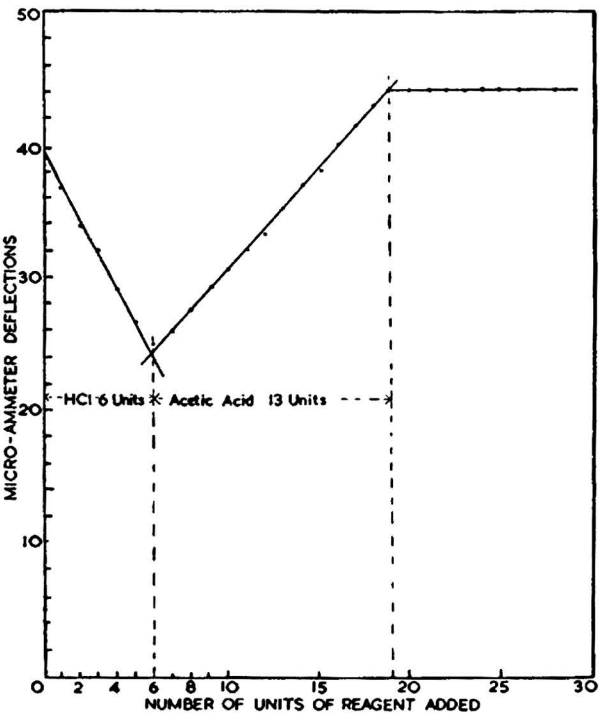


Fig. 4. This graph is for an aqueous solution containing smaller quantities of two different acids, hydrochloric and acetic. The mixture was titrated with 1 *M* ammonia solution in 5-microlitre units

The graphs of Fig. 2 were all obtained with the zero-shunt adjusted to give a normal zero reading on the micro-ammeter when the conductimetric tube was empty. It was found, however, that if the meter zero was set back by adjustment of the shunt, the sensitivity could be again increased and Figs. 3, E and F, illustrate this point. They were obtained with the same concentration of solution as Fig. 2, D, but with meter zero set-back.

The amount of negative zero set-back can be gauged in the following manner. First, with the zero set at its normal position, the conductimetric tube is filled with solution and the coupling condenser is adjusted to obtain a reading. If the deflection is then returned to zero by zero-shunt adjustment the actual zero will have shifted by that amount to the minus side of normal. In order to obtain larger negative zero settings the process is repeated, several times if necessary.

Should the micro-ammeter have a central zero-scale, the first negative readings can, of course, be read directly from its scale, and when that limit has been reached the foregoing process should be applied.

J, in Fig. 1, is the usual resistance controlling the range of the meter. When making negative zero readings the author has found it advisable to keep the meter heavily short-circuited by closing switch M, or better still by means of a key which is only released while there is solution in the conductimetric tube and actual readings are taken.

Fig. 3, F, is a graph for the same solution concentration as for graphs D and E, but was plotted after a further negative zero set-back.

In each case, after the negative setting had been made, the deflection for the solution was again brought forward to 40 μa. by tightening the coupling.

From the foregoing it will be seen that negative zero adjustment makes it possible to titrate extremely dilute solutions.

It is obvious that the graphs here reproduced do not cover anything like the whole range possible; however, the graph F, Fig. 3, has already reached a sensitivity sufficient to enable the operator to dispense with graphs and to obtain sufficiently accurate results for many practical purposes by merely counting the number of units added before the conductivity of the solution takes an upward turn, and there is no reason why the sensitivity should not be still further increased by further negative bias.

Fig. 4 is a graph measuring the quantities of two acids in aqueous solution. To 50 ml. of distilled water were added six 5-microlitre units of 1 *M* hydrochloric acid and also thirteen units of 1 *M* acetic acid. This mixture was then titrated with 1 *M* ammonia added in 5-microlitre units. As can be seen, the quantities of both these acids are confirmed by the graph.

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Department of Physics
University of Sydney
Australia

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Some Applications of a Modified Technique in Paper Chromatography

By L. Rutter

Synopsis—A modified technique in paper chromatography whereby components of mixtures are separated into circular zones, is described, together with resultant advantages, such as speed, simplicity of apparatus and reproducibility. Some new methods of detecting colourless adsorbates are outlined, and examples given of the application of the technique in the analysis of dyes, biological materials and inorganic substances. The possible importance of solubility considerations as a guide to choice of developers is discussed.

In a previous communication[1] a brief description was given of a new technique in paper chromatography, by means of which the substances under analysis are separated into circular zones, instead of the usual spots or bands. The present paper is intended to provide fuller details of the practice, applications and advantages of this method.

According to the technique, two parallel cuts, about 2 mm. apart, are made from the same edge up to the centre of an 11-cm. circular filter paper, and the "tail" so formed is bent at the joint perpendicular to the plane of the paper and cut down to approximately 1·5 cm. in length. Care must be taken to ensure that the parallel cuts are equal in length, otherwise the "tail" will not be squarely perpendicular to the plane of the paper and development may not be truly circular.

The solution to be analysed is then placed as a drop on the joint and generally air-dried. The "tail" is then immersed in developing solvent contained in a small capsule inside a Petri dish, the sides of which support the filter paper in a horizontal plane. A glass plate,

which may be engraved with a suitable scale to assist in following the course of development, is then placed on the filter paper to retard evaporation. Alternatively, the filter paper is sandwiched between two glass plates, the lower one being perforated to accommodate the "tail." The author has found it generally satisfactory to use No. 3 Whatman papers, but for special purposes No. 1 or No. 5 may be more suitable. Filter papers that are acid in their reaction have not been found satisfactory as a general rule.

By capillarity, the solvent rises, and the rate of development may be readily controlled by varying the distance between the liquid surface and the plane of the paper. Solutions containing coloured constituents, suitably developed, give sharp separations into individual zones.

In the case of colourless chromatograms, after development a test sector is cut out and pressed between filter papers impregnated with reagents giving coloured products with constituents of the chromatogram, or sprayed with reagent solution. Preparation of derivatives on the main chromatogram, which may be undesirable, is thereby avoided. Other methods of locating colourless adsorbates are described below.

After their positions have been marked on the main chromatogram and this has been dried, the various bands may be cut out as circular strips and each of these conveniently prepared for elution by placing both ends on filter paper soaked in eluent. Capillary action concentrates the adsorbate in the centre of the strip, whence it may be drawn off by paper or by capillary pipette.

The apparatus is illustrated in Figs. 1 and 2, and a suitable arrangement for concentration of the adsorbates, prior to elution, is shown in Fig. 3. In the latter, the excised strip of filter paper is supported on a pile of three or four micro slides placed in a Petri dish with the ends of the strip touching a small wad of filter paper soaked in eluent. If desired, several strips may be simultaneously treated, the whole being conveniently enclosed by an upper glass plate or inverted Petri dish.

In common with other paper techniques, only very small quantities of materials are necessary for analysis, the method in many cases having a sensitivity of approximately 1 μg. or less of solute. The present technique, however, frequently shows some advantages over the sheet technique of Consden, Gordon and Martin,[2] or the strip methods of Lederer,[3] and Linstead,[4] for the following reasons.

(1) *Speed of separations*—For most separations so far investigated, development to a circle of diameter 6 cm. or less is sufficient and this seldom takes longer than 10 minutes. In contrast with other methods the rate of feed may be accurately and readily controlled by "tail" width and height of paper above the developer surface. Thus, for relatively viscous liquids, such as butyl or *iso*-butyl alcohol, which are slow-feeding, the capsule should be filled to bring the surface within 0·5 cm. approximately of the plane of the paper. As the plane of the paper is horizontal, the feed rate is constant and there is no danger of "water-logging" by syphoning.

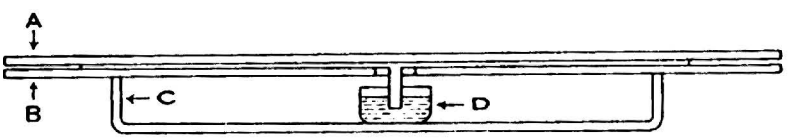

Fig. 1. Sectional view of Apparatus

A = Upper engraved plate B = Lower perforated plate C = Petri dish
D = Container for developer

(2) *Sharpness of separations*—It has usually been found that zones are better defined than the spots or bands obtained by the sheet or strip technique, one reason for which is that there is no blurring of edges, since the zones are circular. Front, and frequently rear boundaries, are also usually sharp and zones are thereby more cleanly separated.

(3) *Testing during development*—A further advantage of the method is that a number of test sectors may be removed at intervals, without upsetting the course of development; this dispenses with the necessity for duplicate or replicate runs.

(4) *Simplicity of apparatus*—A Petri dish and filter paper are the only essentials: the upper engraved glass plate and the lower perforated plate are convenient, but the latter may be dispensed with and an inverted Petri dish serves equally well in place of the upper

plate, if this is not readily available. The developer may be placed in the lower Petri dish, but a small capsule or similar container has advantages and a glass phial of the type used for tablets, cut down to a depth of 1 cm. is more convenient as a container for the developer.

(5) *Compactness*—The apparatus occupies very little space and may thus be placed in a thermostat or refrigerator, if desired. Its small size and portability also render it suitable for enclosure in cabinets, illuminated by ultra-violet or other light.

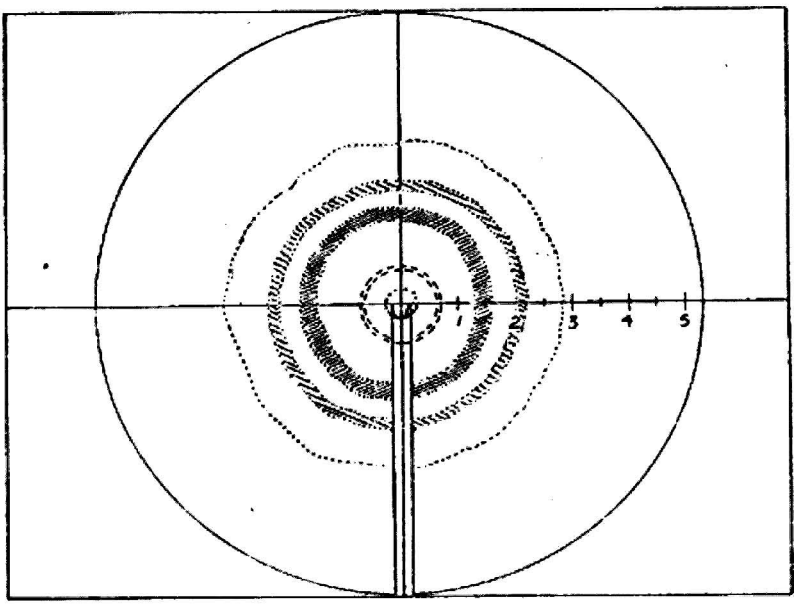

Fig. 2. Plan of apparatus, showing Chromatogram in process of development

LOCATION OF ZONES AFTER DEVELOPMENT—

With coloured compounds, zones are self-indicating, but the location of colourless adsorbates may be more difficult. Many useful methods have been described in the literature, among them the brush technique of Zeichmeister,[5] spraying with specific reagents giving coloured compounds,[6,7] examination under ultra-violet light[8,9] and the use of dyes or other coloured substances, whose behaviour, relative to some constituent of the mixture under analysis, is known.[10]

Some further methods that the author has found useful are based on the utilisation of various factors, among them the following.

(1) *Charring*—The presence of an adsorbate affects the temperature at which the paper chars, and by exposing a test sector to progressively higher temperatures, bands frequently become visible, particularly if examined under ultra-violet light, during heating. It should be noted that some papers contain fluorescent material, which may be removed by a preliminary washing.

(2) *pH Changes*—The pH values of adsorbates may differ from that of the paper, and spraying with dilute solutions of indicators, particularly Universal indicators, is frequently of assistance in showing the positions of the bands.

(3) *Changes in adsorptive properties of the paper*—Adsorbates may alter the adsorptive properties of the paper, and by exposure of a test sector to acid or alkaline vapours, after spraying with indicator, differences in the intensity and shade of indicator colour developed at different parts of the chromatogram, may reveal the location of zones. Exposure to dilute acid fumes, after alkaline vapour treatment, and *vice versa*, frequently affords a sensitive means of differentiation. Spraying with starch solution, after exposure to iodine vapour, is suggested and, if necessary, subsequent treatment with gaseous sulphur dioxide, for closer differentiation.

(4) *Changes in light transmission and reflection*—In the case of hydrophobic adsorbates, bands may sometimes be detected by spraying the paper with water: when viewed by transmitted light, adsorbates show as darker zones which are lighter by reflected light. Such effects may sometimes be enhanced by the use of liquids of different refractive index, such as glycerol, in place of water.

The central feed technique is applicable to separations in various fields, and some typical examples (which are merely illustrative and not intended to be fully comprehensive) are given below.

(*a*) PLANT EXTRACTS—

Many constituents of plant leaves and petals can be rapidly separated by the above technique. In the case of Californian Poppy (Eschscholtzia), an extract of the petals is made with alcohol and ethyl ether and a drop, after drying on the paper, is developed with light

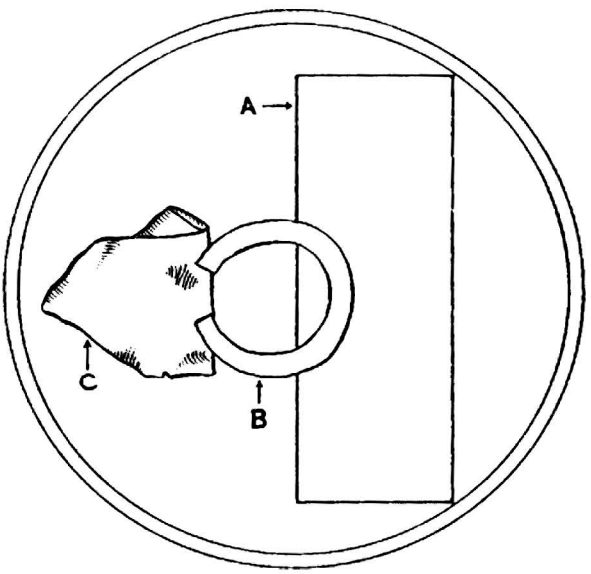

Fig. 3. Arrangement for concentration of adsorbates

A = Micro slides to support excised strip
B = Excised strip
C = Wad of filter paper soaked in eluent

petroleum (b.p. 40° to 60° C.). As many as seven different zones can be detected without further treatment and by exposure to iodine vapour, followed by spraying with starch solution, other bands become visible.

Constituents of grasses may be extracted with a mixture of alcohol, ethyl ether and chloroform and a drop of the extract developed, after drying, with light petroleum. At least three zones become visible, namely, a central green zone consisting largely of chlorophyll, a deep orange zone close to this and a yellow zone at the solvent front. On exposure of the paper to iodine vapour followed by spraying with starch solution, other zones become visible.

A rapid qualitative test for ascorbic acid in plants or artificially prepared mixtures such as vitamin tablets, may be carried out as follows. The material under test is ground with a pestle and mortar, with a little water if necessary, and a drop of the crude extract (which need not be freed from fibrous or other materials), is placed on the centre of a prepared paper and developed with water to a circle of diameter approximately 3 cm. The paper is then gently dried and sprayed with ammoniacal silver nitrate solution. If ascorbic acid is present it will react in the cold with this reagent to give a grey or black band of silver at the former position of the solvent front. Sugars do not interfere with this test, as they reduce this reagent only on heating.

(*b*) DYES—

Many mixtures of dyes can be separated on paper chromatograms and much useful information concerning purity or identity quickly obtained. As a general rule, very dilute solutions (of about 0·1 per cent. concentration) should be used, and water or salt solutions as developers. In the case of Edicol Green (I.C.I., Ltd.), development with water failed to separate the constituents, the band moving with the solvent front, but development with 1 per cent. sodium chloride solution resolved the mixture satisfactorily into a yellow band near the centre and a blue band beyond this. Ammonium sulphate solutions of various concentrations may also prove useful in certain cases. If the dyes are very strongly adsorbed with water alone, the use of dilute acids or alkalis for development may give more satisfactory results. Sometimes solutions of more strongly adsorbed compounds may be used with advantage as developers. For example, a mixture of Chlorazol Fast Scarlet 4B150, Chlorazol Brown LF150 and Chlorazol Yellow G200 (I.C.I., Ltd.), which proved difficult to separate by other means, was satisfactorily resolved by development with a 0·025 per cent. aqueous solution of cetyltrimethyl ammonium bromide. If it is undesirable to use salt solutions, "partition" methods in many instances may be recommended; *e.g.*, Edicol Green developed with *iso*-butyl alcohol saturated with water separates well into its components.

(*c*) INORGANIC SEPARATIONS—

By taking advantage of complex formation many cations may be separated. For example, one drop of an 0·1 per cent. solution of mixed copper and iron nitrates may be developed with water to a circle of diameter approximately 2 cm. and then exposed to ammonia vapour and developed with a dilute solution of ammonia containing ammonium chloride. The iron is precipitated on exposure to the ammonia vapour, whereas the complex cuprammonium compound moves with the solvent front on further development. Spraying a test sector with potassium ferrocyanide solution reveals the position of the zones, whose presence may also be shown by "charring" a test sector. Cobalt and nickel may also be separated by development with dilute ammonia, test sectors being treated with the appropriate reagents.

The "extraction" methods for inorganic separations described by Linstead and his collaborators[4,11] may be carried out by the central feed technique and in many instances show advantages over the use of single solvents for development.

CHOICE OF DEVELOPERS—

The success of chromatographic separations depends largely on the solvents used, and some guide to choice may be obtained from considerations of polarity and solubility. It is generally recommended in the literature [12,13] that non-polar or only slightly polar liquids should be used for development, but solubility effects, which are seldom mentioned, may have an important bearing and should be considered. For example, anthracene and fluorescein may be rapidly separated by development with water containing 5 per cent. of ethyl alcohol, a mixture in which anthracene is less soluble than fluorescein, although water is highly polar. Alternatively, development with light petroleum, in which anthracene is the more soluble, also leads to separation, the fluorescein being preferentially adsorbed. Some fluorescent constituents of a sample of complex tarry material, which were eluted when development with light petroleum was attempted, were satisfactorily resolved by development with alcohol, in which they were less soluble.

Certain proteins and dyes may be separated by the use of salt solutions in which they are less soluble than water, as suggested by Tiselius.[14]

It would appear that solvents in which the substances to be separated show the greatest difference of solubility are desirable and that for adsorption of non-polar or only slightly polar compounds a solvent in which they have a low solubility is preferable.

Investigations of the physical factors affecting chromatographic separations on paper are facilitated by the reproducibility that is a feature of this method, and a study of the effects of polarity of solvent, surface tension, activation of paper and possible electrical effects[15] is in progress and will be reported elsewhere.

The author wishes to express his indebtedness to Mr. D. W. Wilson of the Sir John Cass Technical Institute, and Dr. J. H. Hamence for helpful discussions of this work, and to Messrs. I.C.I., Ltd., who kindly supplied various dyestuffs.

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

May, 1949

Investigations in the Examination and on Variations in the Composition of Milk

Part I. The Determination of the Hortvet Freezing-Point

BY R. W. SUTTON, J. MARKLAND, A. BARRACLOUGH AND W. B. CHAPMAN

SYNOPSIS—Some difficulties in the determination of the freezing-point of milk by the Hortvet method are discussed. Possible sources of error are enumerated, some of which are thought to be inherent in the apparatus, and it is shown that these errors can be reduced to low proportions by the adoption of a carefully controlled technique, which is particularly necessary in the standardisation of the thermometer with sugar solutions.

IN the examination of samples of milk the determination of the freezing-point is a test which has received considerable attention since Hortvet described an apparatus suitable for routine work, and more particularly in this country following the work of Elsdon and Stubbs. The importance of an accurate result can hardly be over-emphasised, for the test has come to be regarded as one that enables a true distinction to be made between milks naturally deficient in non-fatty solids and those containing added water. The action of a Food and Drugs Authority may therefore depend on the result. Correct figures are also important in compiling records if these are to be of value. It is clear that if any worker is regularly recording figures for the Hortvet freezing-point depression* which are incorrect, he will either report a rate of milk adulteration which is higher than the truth, or alternatively he will report a greater proportion of milks showing a natural deficiency in non-fatty solids than would be reported with correct Hortvet results.

In his original paper, Hortvet[1] reviews earlier work on the freezing-point of milk and describes a cryoscope suitable for routine work. He states that "the thermometer should be carefully standardised and calibrated in comparison with a U.S. Bureau of Standards tested instrument." There is no mention in this paper of the use of sugar solutions. These were apparently first used in further collaborative work whilst Hortvet was Referee on Dairy Products.[2] The sucrose solutions (7 and 10 per cent. w/v) originally used in collaborative work were later adopted by the A.O.A.C. as the basis for standardisation of the thermometer, and they are specified in the present official method.[3] It must be assumed that the freezing-point depressions (*viz.*, 0·422° and 0·621° C.) accepted by the A.O.A.C. for these two sugar solutions were those obtained when the most accurately calibrated thermometers available

* It is usually convenient to refer to freezing-point depressions rather than actual freezing-points, and unless otherwise stated in the text, this practice will be followed in this paper.

were used in the Hortvet apparatus and with the Hortvet technique, *i.e.*, with no corrections for super-cooling or heat transference. Elsdon and Stubbs[4] record that they ascertained that the two thermometers used would be correct to about 0·002° to 0·005° C. It should, however, be emphasised that whilst Hortvet's figures may not be strictly correct, they form the real basis for all "Hortvet" results. All our records rest on the assumption that 7 per cent. w/v sucrose solution when examined by the Hortvet method gives a depression of 0·422° C. and that 10 per cent. sucrose solution gives a depression of 0·621° C. If this is accepted it seems clear to us that the actual apparatus used is unimportant, provided that the thermometer is a satisfactory one and that with the apparatus chosen it is possible to obtain reproducible results. Any alterations in apparatus or technique to improve the reproducibility of the results, although possibly representing a departure from the process originally described by Hortvet, may be adopted without objection and the results may properly be classed as "Hortvet results" if in the standardisation Hortvet's figures for 7 and 10 per cent. sucrose solutions are accepted.

The object of this paper is to record our conclusions following an extensive experience in using the Hortvet method, to refer to factors which in our opinion can be responsible for some lack of agreement in the results obtained by different workers, to emphasise the need for a more comprehensive standardisation of the thermometer than is adopted by some workers and to recommend the adoption of a very rigid technique.

Difficulties and possible sources of error

(*a*) Use of sugar solutions—

In the A.O.A.C. official method, 7 and 10 per cent. sucrose solutions w/v are still specified for the standardisation, and as pointed out by Stubbs and Elsdon[5] the accuracy of the correction to be applied to any recorded figure depends on the assumptions that there is equidistant spacing of the graduations between the two freezing-points recorded and that the bore of the thermometer is uniform between these two points. These assumptions may not be correct.

There is further some difficulty in obtaining really concordant results for the freezing-point of sugar solutions, and this difficulty has been referred to by previous workers. In the collaborative work undertaken when sugar solutions were first used[2] there is the instruction not to include adventitious results "which are in marked disagreement with other results obtained by carefully following instructions," and this direction is included in the official A.O.A.C. method to-day. Elsdon and Stubbs[4] refer to it. They encountered variations up to 0·005° C. with sugar solutions, but state that by making a sufficiently large number of determinations it is possible to obtain a figure that can be accepted as correct. We agree with this but, from our conversations with other workers, we doubt if this possible source of error is generally appreciated. Further, although occasionally results are obtained which "are in marked disagreement with other results obtained by carefully following instructions" it sometimes happens that the results are spread evenly over a relatively wide range, and in these circumstances, in our opinion, an average figure cannot properly be accepted as correct. Accurate results can be obtained only if this variability is reduced to really low proportions. In our opinion this can be done by strict control in the experimental technique.

At an early stage we decided that a better standardisation with sugar solutions than that specified by the A.O.A.C. was necessary, and indeed it has been our practice for many years to standardise thermometers when first used and at about two-year intervals in considerable detail with sugar solutions of intermediate concentration as well as the 7 and the 10 per cent. solutions. We also check at more frequent intervals with 8·75 per cent. w/v sugar solution ($\Delta = 0{\cdot}536–7°$ C.). "Hortvet" figures for these intermediate strength sugar solutions have been computed by Stubbs and Elsdon.[5] Corrections to be applied between the temperatures recorded for the seven sugar solutions are obtained by interpolation. There is obviously less error in assuming uniformity in the bore and in the graduations of the thermometer for the smaller intervals.

In our work with these sugar solutions of concentrations ranging from 7 to 10 per cent. we have found in two separate cryoscopes that the spread of results is more marked with the stronger solutions. Indeed, there is almost a regular decrease in reproducibility with increase in the concentration of the sugar solution under examination.

In Table I figures are included which show the gradual increase in the spread of the results with increasing sucrose concentration. These results were obtained after close standardisation

of the experimental technique (referred to later), and greater variations have been recorded with insufficient attention to detail.

TABLE I

PER CENT. SUCROSE SOLUTIONS W/V

	7·0	7·5	8·0	8·5	9·0	9·5	10·0
No. of readings ..	12	12	12	12	30	12	12
Average depression, °C.	0·4144	0·4457	0·4771	0·5095	0·5420	0·5752	0·6087
Difference between extremes, °C. ..	0·002	0·0025	0·003	0·0015	0·004	0·003	0·004
Standard deviation, °C.	±0·0007	±0·0008	±0·0010	±0·0005	±0·0011	±0·0010	±0·0013
Theory, °C. (Stubbs and Elsdon[5]) ..	0·4220	0·4543	0·4870	0·5200	0·5532	0·5869	0·6210
Correction, °C. ..	+0·0076	+0·0086	+0·0099	+0·0105	+0·0112	+0·0117	+0·0123

(*b*) FACTORS AFFECTING THERMOMETER READINGS—

There are several uncontrolled factors which affect the thermometer readings. Their effects are to be seen in the variations in the ice-point, but clearly they are included in all readings. The factors to which we wish to draw particular attention are additional to those

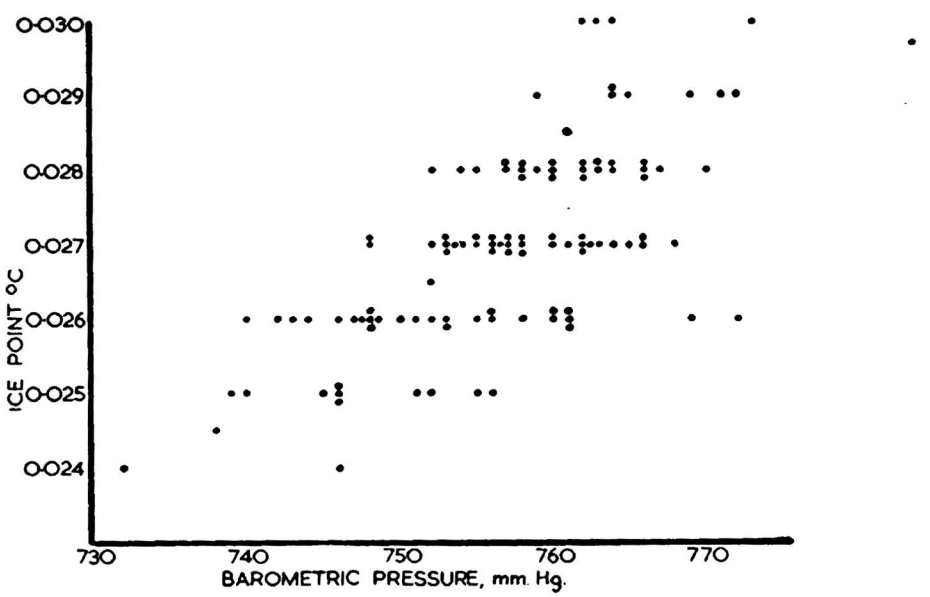

Fig. 1

gradual changes which have been recorded in newly made thermometers and which may persist over a period of years. They may conveniently be divided into three categories—

(i) *Pressure effects*—The true freezing-point of water or of an aqueous solution is slightly depressed by an increase in pressure. In practice considerable changes in the ice-point of a Hortvet thermometer do occur from one day to another, and previous workers[6] have recorded that this variation is correlated with atmospheric pressure. The correlation is, in fact, a positive one and is, of course, due to the thin-walled thermometer bulb being compressed by increase in atmospheric pressure and forcing the mercury further up the capillary.

Observations of the freezing-point of distilled water in one apparatus, recorded at different atmospheric pressures, over a period of some months are illustrated in Fig. 1. The correlation coefficient is +0·68 ±0·05.

(ii) *Temperature effects*—In the Hortvet apparatus there is a certain length of the column of mercury exposed to atmospheric temperature and any variation in this temperature will

cause an alteration in the reading. We have calculated that for the mercury column exposed in an ice-point determination the reading will change by about 0·0003° C. per degree centigrade change in atmospheric temperature. The corresponding figure for a depression of 0·5° C. is about 0·0002° C. An ice-point determination immediately before or after the determination of the freezing-point of a milk sample will compensate for the effect of external pressure and for the bulk of the temperature effect, but it is clear that if the ice-point and the freezing-point of a milk sample are determined at different conditions of room temperature an error will be introduced.

(iii) *Mechanical changes*—We find that Hortvet thermometers show some variation in the ice-point throughout a period of continuous use during the day. The variation is always in the same direction and in our experience there is a gradual rise in the temperature recorded. This does not entirely accord with the experience of Elsdon and Stubbs,[6] who found with one thermometer that there was a tendency for the ice-point to be lower at the end of a day—even when the thermometer had been kept in ice between the readings.

We have regularly observed this alteration in the ice-point during continuous use of a thermometer. The effect is more noticeable in some thermometers than in others. With one thermometer we have recorded a change in ice-point from +0·0205° C. to +0·026° C. in the course of a day. During this period 24 freezing-point determinations had been made.

Most of the change takes place in the earlier stages. Later the change is more gradual and constant readings may finally be recorded. The early part of this change is probably due to a delay in contraction of the glass after being kept at room temperature. The later part may to some extent be due to an increase of room temperature.

The variation may be only small but it is measurable and, in making a long series of freezing-point determinations, we now invariably include several determinations of the ice-point. These are applied to the adjoining results for the purpose of recording depressions.

(*c*) APPARATUS—

From our experience we think that variations in size of different parts of the Hortvet apparatus may indirectly be responsible for some variation in results.

In this laboratory two Hortvet cryoscopes have been in use for some years. They were made by different firms and they differ considerably in the following measurements, which are thought to be important.

	A	B
Diameter of thermometer	9·5 mm.	8·9 mm.
Internal diameter of freezing-point tube	23·2 "	27·0 "
Outside diameter of freezing-point tube	25·9 "	29·6 "
Inside diameter of metal tube	26·7 "	31·7 "
*Clearance of bulb from bottom of tube	11 "	15 "
Volume of liquid used	27·5 ml.	43·5 ml.

* This distance, of course, can be controlled. The figures given are correct for the period when most of the records were made.

It will be seen that the clearance between the tubes (occupied by the alcohol layer) is 0·4 mm. in apparatus A and 1·05 mm. in apparatus B and, probably what is more important, the clearance between the thermometer bulb and the inside of the freezing-point tube (occupied by the solution under test) is 6·85 mm. for apparatus A and 9·05 mm. for apparatus B. In use, apparatus A with the narrower tube and smaller volume of solution is much quicker than apparatus B, but it presents greater difficulty in standardising with sugar solutions. We think that the clearance between the thermometer bulb and the wall of the freezing-point tube is of importance and that a difference in this measurement may easily be the explanation of the greater difficulty in obtaining concordant results on sugar solutions in apparatus A compared with apparatus B. In apparatus A—with the wider thermometer and narrower freezing-point tube—the clearance is less and the effect of the lower temperature of the outer cooling bath is more noticeable. Further, the smaller this clearance the greater would be the effect of any slight out-of-centre position of the thermometer.

That the nearness of the thermometer bulb to the outer cooling bath has an effect on the results can be readily demonstrated by altering the depth of the thermometer in the freezing-point tube. The following results were obtained with a thermometer in different positions and they are recorded in the order in which they were obtained by two workers.

These variations in position, of course, were chosen to exaggerate the disturbance of the results. The greater depressions are undoubtedly due to a more pronounced effect by the outer bath.

	Distance between thermometer bulb and bottom of tube	Reading, °C.	Ice-point, °C.
J. M.	2 cm.	− 0·4975	
			+ 0·027
	¾ "	− 0·4965	
	¼–½ "	− 0·503	
			+ 0·027
R. W. S.	¼–½ cm.	− 0·502	
		− 0·502	
	¾ "	− 0·497	
	1¼ "	− 0·497	
	2 "	− 0·496	
			+ 0·027

(*d*) TECHNIQUE—

In the instructions given in the A.O.A.C. Methods of Analysis it is directed that three stirs shall be given as the mercury approaches its maximum. Whether or not this is intended to exclude all stirring between seeding and the three stirs is not clear.

Stubbs,[7] in investigating the stirring in the Hortvet apparatus, found that there was no significant difference in the result obtained whether the stirring was continuous or as laid down by the Hortvet technique. Indeed, it is suggested that the Hortvet technique might be altered so as to permit of a certain amount of stirring during the ascent of the mercury column.

This led us, and it may have led others, to conclude that the actual amount of stirring and the time of stirring in the Hortvet process were not of major importance. It appears, however, that Stubbs's conclusions were reached following experiments with milk samples only.

In our experience alterations in the amount of stirring have a marked effect on the results with sugar solutions and a less, though measurable, effect when examining milks. With increased stirring the effect is to give a larger depression and the time during which the mercury remains stationary at its maximum is reduced. The effects are more noticeable in apparatus A, with the smaller clearance between the thermometer bulb and the freezing-point tube, where stirring is likely to be more efficient. With this apparatus, if stirring is continued alternately with tapping of the thermometer it is almost impossible to record a result. The mercury rises to a maximum which is considerably lower than is obtained by the usual procedure and immediately falls rapidly.

One further point may be mentioned. Whatever technique is followed, if one or two stirs are given after the steady temperature has been recorded, there is a quick fall of the mercury. This surely means that the outer layers of solution in the freezing-point tube are at a lower temperature and that the thermometer has recorded the temperature of an inner layer only. This cooling effect of the outer bath leading to more formation of ice and a concentration of the solution (with increased depression of the freezing-point) must in fact be going on all the time and the temperature recorded at the final reading represents a balance. It is that point where the heat produced by formation of ice is equalled (and later exceeded) by the effect of the cooling bath. With a limited amount of stirring in the Hortvet process, temperature changes due to these two opposing effects are slow and there is a point where there is no noticeable change in the reading of the thermometer.

We are therefore led to the conclusion that difficulty in obtaining concordant results in the Hortvet apparatus is largely due to the cooling effect of the outer bath, and all our experience accords with the theory of Monier-Williams[8] that steadiness of temperature at the final reading is secured mainly by the fact that stirring is inefficient. Indeed, in our opinion it is absolutely essential to limit the amount of stirring and to adhere to a rigid technique if reasonably concordant results are to be obtained.

In our early experiments we found that final temperatures were steadier (the temperature

being constant for at least a minute with sugar solutions and for several minutes with milk) if three stirs were made immediately after seeding with ice and no further stirring done. The seeding was done at $-1{\cdot}6°$ C., the mercury probably receded to about $-1{\cdot}65°$ C. before rising, three stirs were given at a steady rate during which time the mercury rose to about $-1{\cdot}3°$ C. Tapping of the thermometer was commenced when the movement of the mercury was quite slow.

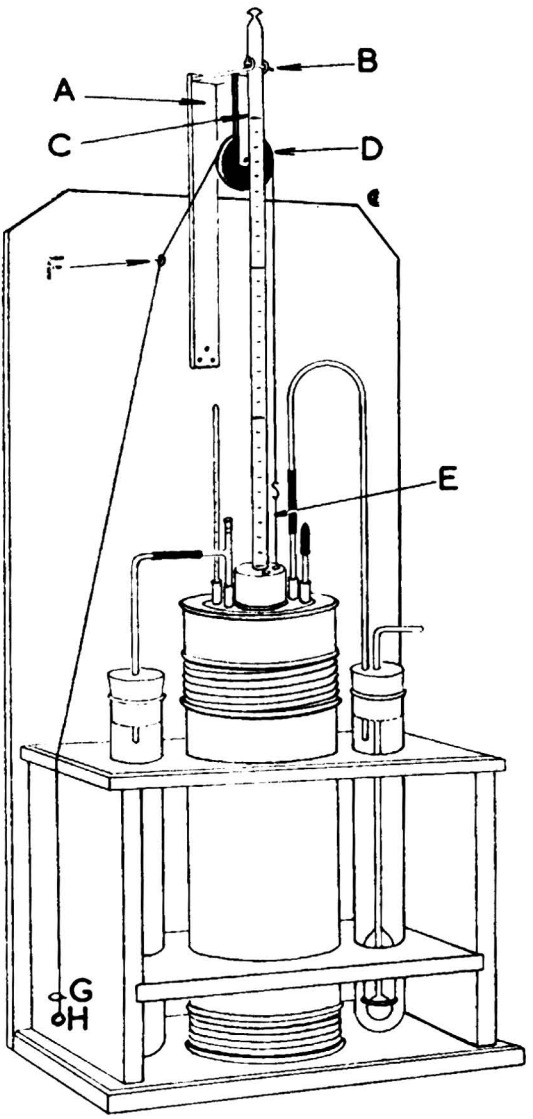

Fig. 2

Later results were somewhat more erratic and we have returned to the technique of giving three stirs at a later stage. We still seed with ice at $-1{\cdot}6°$ C. and manipulate the starter and the stirrer to secure a quick rise of the mercury (in our experience those occasional results which are readily classed as abnormal are always associated with a slow rise of the mercury), stir three times immediately after the mercury has risen past $-1{\cdot}0°$ C. and thereafter do no more stirring. The thermometer is tapped until the reading is constant. With this technique we have obtained rather more concordant results with sugar solutions, but differences are still recorded. We also have the impression that the final temperatures are not quite so steady,

particularly with the stronger sugar solutions. In many instances the maximum rise of the mercury is not maintained for more than half a minute. We, however, prefer this later technique, because of the more concordant results and also because it tends to give a slightly higher rise of the mercury, *i.e.*, a smaller depression.

A convenient stirring device is illustrated in Fig. 2. It consists of a metal bracket attached to the back board of the apparatus. The front part of the horizontal arm is slotted to take the thermometer—this being held in place by a small metal arm. If the bracket is of the right size, the thermometer is thereby held in a safe and perfectly upright position.

Part of the way along the bracket is a metal pillar mounted on a swivel fitting and carrying a pulley wheel. A small S hook is attached to the stirrer and a thread from the S hook passes over the pulley, through an eye hook in the back board, through a second eye hook on the side of the apparatus and is threaded through and secured to a metal bead somewhat larger in diameter than the eye hook. The eye hook at the side of the apparatus is fixed so that the distance above bench level is at least equal to the depth of liquid in the freezing-point tube. The thread length is arranged so that when the metal bead is at its highest level (*i.e.*, next to the eye hook) the stirrer is just resting on the bottom of the freezing-point tube. Under these conditions simple pulling of the metal bead down to bench level provides for complete movement of the stirrer through the liquid being frozen.

Typical results

In Table I are summarised results on our latest standardisation of a thermometer with sucrose solutions (apparatus A). They were obtained by three workers following the recommended technique and all contributed at least three results with each sugar solution. Ice-point determinations were made at intervals throughout each series of tests and applied to the appropriate individual results.

It is clear that individual results for sucrose solutions ought not to be accepted for the purpose of applying corrections, but, from the standard deviations, it is also clear that if a sufficient number of determinations are made on any sugar solution the error need not be large.

We prefer this comprehensive standardisation of the Hortvet thermometer since corrections ascertained at seven points should reveal any serious defect in the bore of the thermometer. After plotting the results, a table may be constructed giving the appropriate corrections to be applied to any result. It is desirable to check the standardisation occasionally and for this purpose 8·5 per cent. or 8·75 per cent. w/v sugar solution may conveniently be used.

Suggested further improvements

If we are correct in our opinion that many of the difficulties with the present Hortvet apparatus are due to the continuous contact between the freezing-point tube and the cooling bath, then it follows that the principle of removing the alcohol layer in the Monier-Williams apparatus is eminently sound.

We have recently conducted further experiments with the Monier-Williams apparatus, particularly to ascertain the effect of differences in technique. We can say at once that in this apparatus the technique employed is of far less importance. The contrast between the Monier-Williams apparatus and the Hortvet cryoscope is indeed quite remarkable. In our experiments with the Monier-Williams apparatus the amount of stirring and the time when this is done are without effect. Stirring can be done immediately after seeding or as the mercury approaches its maximum or throughout the rise of temperature. Indeed, it is difficult even with the 10 per cent. sucrose solution to obtain results which are not in complete agreement. This difference between the two cryoscopes may, of course, be due to several factors. We feel, however, that the isolation of the freezing-point tube by removal of the alcohol layer at the time of freezing must be of chief importance.

The apparatus has disadvantages for routine work of which we are conscious. Because of the larger volumes of liquid to be cooled it is much slower. In our apparatus, 60 ml. of solution are required to immerse the thermometer bulb and 50 ml. of dilute alcohol required in the space between the tubes. A determination requires 20 to 25 minutes. There is more heat loss from the instrument and therefore a greater consumption of ether.

It is therefore difficult to recommend the adoption of the Monier-Williams apparatus for routine testing of milks, but we see no reason why the principle of removing the alcohol layer should not be added to the Hortvet apparatus. This, of course, has already been

tried by Elsdon and Stubbs[4] and not recommended. We are now having a Hortvet cryoscope altered on similar lines, and feel sure that there should be some improvement in the reproducibility of the results with sugar solutions on which the accuracy of all other results depends so much.

As explained earlier, we see no objection to this in principle. Provided that standardisation is carried out on the assumption that in the Hortvet method 7 per cent. sucrose freezes at −0·422° C. and that 10 per cent. sucrose freezes at −0·621° C., a modified apparatus will still give results which are quite properly compared with previous records, some of which have been collected with great care, and there will be no need to alter materially the figures which are to-day accepted as normal for genuine milk.

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County Laboratory
St. Mary's Gate
Derby

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The Determination of Carotene in Dried Peas

By DAVID FRANKLIN, F. B. LYONS and T. S. WHEELER

Synopsis—The powdered sample, containing 14 per cent. of moisture, is extracted by standing for 16 hours with a 2 + 1 mixture of light petroleum and acetone. The extract is evaporated with light petroleum to remove acetone and then passed first through dicalcium phosphate to remove unwanted pigments and afterwards through a mixture of sodium sulphate and alumina to adsorb the carotene, which is eluted with a 1 to 1·2 per cent. solution of acetone in light petroleum and estimated absorptiometrically as β-carotene in the eluate.

Statistical interpretation of the results of an experimental study of its various stages indicates that the method is efficient in that there is a linear relationship between the quantity of pea-flour taken and the quantity of natural carotene found. The results at the 95 per cent. level for a 4·3-g. sample are accurate to within ±5 per cent. of the carotene present. There is evidence that pea-flour contains an anti-oxidant which stabilises carotene during the removal of acetone from the first extract.

In recent years much work has been carried out on the estimation of carotene in plant and food material by chemical and physical means. Less attention has been paid to the accuracy of the methods used, even when this would appear desirable, for example, with dried peas where minute quantities (about 3 to 4 p.p.m.) of the pigment are involved. This paper describes a chromatographic method of estimating carotene contents of the order of 3 p.p.m. in dried peas and includes a statistical examination of the accuracy of the results. Figures for the carotene content of peas in various forms—fresh, frozen, canned and blanched—have been published by a number of authors,[7,15,16,22,24,40,48, etc.] and the statistical treatment of carotene contents have been discussed[7,8,10,14,22,24,30,40,41, etc.] No attempt has been made in the present work to distinguish between the constituents of the total crude carotene obtained, which has, as is usual, been determined as β-carotene.[3,7,18,20] Kemmerer[18,20] has suggested using the plural, carotenes, for the mixture of carotene isomers that is estimated, but we prefer the singular, carotene, which is used throughout this paper in a general sense, and includes mixtures of carotenes of unknown composition.

Method used for the determination of carotene

A number of general discussions of the estimation of carotene have appeared in the literature.[7,25,49] For the purpose of the present research there was required a rapid process

of estimation that would give with dried peas results suitable for statistical treatment. The following method, based on a combination of known and tested procedures for extraction, chromatography and photometric determination of carotene, was developed after a number of trial experiments; eight to ten results can be obtained with it in a working day.

Extraction—The extraction of carotene has been made the subject of frequent discussion.[1,2,3,4,7,11a,27,28,36,37,42,44,49] The technique employed was similar to that described in [36] and [44]. A sample (about 4 g.) of marrowfat peas, dried at 44° C. to 14 per cent. moisture content, was ground to pass a 60-mesh sieve. Except in the experiments listed under Group E below, all such samples were taken from a master sample (7 lb.) of the marrowfat peas. The moisture content (14 per cent.) was checked at intervals. The ground material was kept in the dark[7,33] at room temperature for 16 hours in contact with a mixture of 40 ml. of light petroleum (b.p. 40° to 60° C.) with 20 ml. of A.R. acetone. The latter solvent was removed from the decanted extract and washings (light petroleum, b.p. 40° to 60° C.; two lots of 50 ml.) by evaporation at 100° C. to 15 ml.; fresh light petroleum (50 ml.) was added and concentration to 15 ml. repeated.[44] This procedure causes some isomerisation of β-carotene, but the effect is small,[3,4,35,36,42,45,46] as shown by the results of recovery tests (see Table I). The solution of carotene and other pigments in light petroleum (15 ml.) thus obtained was diluted with light petroleum to 40 ml. before recovery of the pigments.

Chromatography—The chromatographic method for the separation of carotene is now more popular than the phasic method.[1,3] A two-stage process[34] was employed, dicalcium phosphate[27,29] being used in the first, and sodium sulphate - alumina mixture[7] in the second column. The additional stage was found useful for concentration of carotene prior to determination, and also as a check on the activity of the first column. Dicalcium phosphate (see [26] for the use of bone meal), is satisfactory for the removal of contaminating pigments from carotene, but its activity is liable to change so that a second guard column is on the whole advisable.[3,7,34] Further, the phosphate is not specific for the removal of chlorophyll.[42]

In the preparation of the first column, dicalcium phosphate was placed in a glass tube, 32 cm. long by 1·0 cm. internal diameter, constricted at one end, plugged there with cotton wool and connected to a receiver through suction.[7] A slurry of the dicalcium phosphate with light petroleum was introduced and further adsorbent was added intermittently with intermediate suction. When the adsorbent reached a length of 15 cm., it was capped with a 1-cm. layer of anhydrous sodium sulphate. The level of light petroleum was maintained above the sulphate at all times. The second column, 19·0 cm. long by 1·0 cm. internal diameter, which was used as described in [7], was filled to a height of 7 cm. with a mixture of sodium sulphate and alumina; the value of alumina in avoiding the necessity for saponification is discussed in [5,7,17]. Neither column was employed more than twice, and not if over a few hours old. Changes in activity were indicated by the behaviour of the columns; in particular the dicalcium phosphate did not adsorb all chlorophyll, and the adsorption band of carotene on the alumina appeared diffuse.

The prepared extract was transferred to the first column, and two 10-ml. portions of light petroleum were used for washing. When about 1 cm. of washing liquid remained over the sodium sulphate surface, carotene and possibly some chlorophyll were washed through with light petroleum (50 ml.); other interfering pigments remained on the dicalcium phosphate.[27]

The solution of carotene in light petroleum, amounting to about 110 ml., was poured on to the second column where the pigment was adsorbed as a diffuse orange band (0·5cm.) at the top. Booth's eluting solution[7] (1·2 to 2 per cent. by volume of acetone in light petroleum) was added, and the eluate, about 7 ml., containing carotene was made up to 10 ml. with light petroleum. Usually four lots (about 4 g. each) of one sample of peas were examined at one time, using two columns of each adsorbent.

Estimation of carotene—The crude carotene content[20] of the resulting solution was estimated as β-carotene by means of a Spekker photo-electric absorptiometer fitted with a filter giving maximum transmission at 450 mμ.[12,19] and calibrated with β-carotene at various concentrations (0·2 to 2·0 p.p.m.) in light petroleum (b.p. 40° to 60° C.). Neither a visual photometer nor a colorimeter using aqueous potassium dichromate as standard was found satisfactory[30,47] with the carotene concentrations involved. The standard sample of β-carotene ($E^{1\%}_{1\,cm.}$ = 2310 at 464 mμ. in benzene)[12] was kindly supplied by Messrs. Lever Brothers and Unilever Limited (Dr. G. C. Hampson and Dr. R. F. Hunter). It was stored in the dark at 0° C. in an atmosphere of carbon dioxide.

Details of Experiments

Recovery of β-carotene in relation to various stages of the routine procedure (see table I)—

These experiments, which were preliminary to the main work (groups E and F below), involved the determination of the percentage recovery of added β-carotene from—

A: pea-flour which had been previously stripped of pigments,
B: a 2 : 1 mixture of light petroleum and acetone by volume,
C: the adsorbents (dicalcium phosphate followed by sodium sulphate - alumina mixture),
D: stripped pea-flour to which quinol had been added.

These trials were designed to yield information in regard to losses of carotene due to—(A) incomplete extraction from the material; (B) loss during the evaporation of acetone from the pigment extract; (C) incomplete recovery from the adsorbents. In the (D) series the protective (anti-oxidant[7,44]) effect of quinol was examined.

Experimental methods—

The calibrated photo-electric absorptiometer fitted with a filter as described above was used to standardise a β-carotene solution of suitable concentration in light petroleum (b.p. 40° to 60° C.) (*cf.* reference 2, p. 600). This solution was employed to provide in replicate the quantities of β-carotene required for the recovery trials.

A—Trials—The pea-flour used was ground to pass 60 mesh and stripped of pigments by extraction with acetone until colourless, and air-dried. Quantities of β-carotene in light petroleum (about 10 ml.) corresponding to the quantity of carotene found in the unextracted pea-flour (about 3 p.p.m.) were mixed with the stripped air-dried flour samples (about 4 g.) contained in conical 150-ml. flasks and light petroleum and acetone were added to make up the prescribed extracting solvent. The stoppered flasks were kept overnight in the dark, and carotene was estimated by the complete routine procedure.

B—Trials—Amounts of β-carotene of the same order as present in pea-flour, and of five and ten times those amounts, were kept overnight in stoppered flasks in the prescribed quantity (60 ml.) of solvent, and the routine procedure for estimation was followed from that stage onwards.

C—Trials—The amounts of β-carotene used in the A—Trials were dissolved in light petroleum (10 ml.) and added to a column of dicalcium phosphate prepared as described above, and the remainder of the routine estimation procedure was followed.

D—Trials—The procedure was as described for the A—Trials with the modification that the addition of quinol in light petroleum (10 ml.) to the stripped pea-flour preceded that of β-carotene.

Table I

Recovery of β-carotene in relation to various stages of the routine procedure

Trial series	Number of estimations	β-Carotene added in individual estimations, μg.	Recovery (%) of added β-carotene: Max.	Min.	Mean	Average amount of β-carotene lost μg.	Coefficient of variation of results
A (Stripped pea-flour) ..	8	12·9	92·2	82·2	87·3	1·6	4·33
B1 (Extracting solvent) ..	10	12·9	91·4	82·0	86·7	1·9	3·63
B2 (Extracting solvent) ..	10	70·8	93·2	86·7	90·3	6·9	2·49
B3 (Extracting solvent) ..	10	132·8	93·4	90·4	91·6	11·2	1·04
C (Adsorbents)	10	11·0	100·0	92·7	95·6	0·5	2·05
D1 (Stripped pea-flour and quinol)	7	26·5 + (1·2 μg. quinol)	98·1	88·7	94·1	1·5	3·71
D2 (Stripped pea-flour and quinol)	7	20·3 + (3·5 μg. quinol)	96·1	90·1	94·0	1·2	2·31

It will be seen that the recoveries in trials A and B1 are substantially identical, from which we infer that the carotene loss (about 13 per cent.) is unlikely to be due to incomplete extraction from the pea-flour. From trials B1, B2 and B3 it is seen that recovery from the

solvent is to some extent a function of the amount present, and that the greater the concentration of carotene, the better and less variable the recovery, from which it must be concluded that the accuracy of the method is necessarily limited by the low level of carotene normally present in dried peas.

Trial C gave recoveries significantly higher (nearly 9 per cent.) than trials A and B1, which indicates that the excluded stage in trial C (the evaporation of the petroleum acetone) must be responsible for this difference. It also seems that chromatography accounts for more than 4 per cent. loss of carotene under these conditions. Hence the over-all loss of 13 per cent. is divided between the two main stages. But it is also seen from trials D1 and D2 that this 13 per cent. can be reduced to 6 per cent. by the addition of quinol. The protective (anti-oxidant) action of quinol and related compounds on carotene is of course well known.[6,7,31,37,38,39,43,44]

These conclusions are supported by the results of application of the F- and *t*-tests[11,13,32] to the experimental data.

Accuracy of estimation of carotene in pea-flour

After completion of the preliminary experiments on the various stages of the procedure, the accuracy of the method of estimation was examined in five independent sets of experiments divided into two groups, E and F. Group E, which related to one batch of peas, comprised three sets, in two of which known weights of carotene were added to weighed pea-flour samples before applying the routine analytical procedure. In the third set, carotene was not added before estimation. The second group, F, which was based on the master-sample batch of peas, involved two sets only, in one of which carotene was added before estimation. Table II summarises the relevant data.

Table II

Group	Set	Number of samples in set	Range of sample weights		Wt. of carotene added,	Range of results for carotene originally present in p.p.m.		
			Max.	Min.		Max.	Min.	Mean
			g.	g.	μg.			
E	E_1	4	5·75	4·04	8·2	4·06	3·74	3·88
	E_2	12	4·70	4·04	5·8	4·82	3·60	3·93
	E_3	16	5·61	3·71	0	4·39	3·01	3·71
F	F_1	8	4·91	3·93	12·8	3·35	2·75	3·11
	F_2	8	5·00	3·55	0	3·31	2·87	3·04

The experiments included in group E differed from those in group F in that the absorption readings for group E were made on a different absorptiometer housed in a building about 400 yards distant from the laboratory, so that it was necessary to carry the solutions of carotene in light petroleum between the buildings.

The methods of regression analysis (see reference 11, p. 118) were applied to the five independent sets of experiments. It was found that the results in both E and F could be expressed by an equation of the form $Y = A_0 + A_1X$, where Y is the natural carotene content in μg., and X is the weight of the sample taken. A_0 has the values 2·58 and −0·94 and A_1 the values 3·24 and 3·29 for group E and group F respectively. The two values for A_1 do not differ significantly, but there is a significant difference in the A_0 values, although each of these values is not significantly different from zero. It is of course to be expected that Y and X will vanish together.

The analysis also shows that, taking a 4·3 g. sample as standard, the carotene content of the group E samples at the 95 per cent. level of probability is 3·8 ± 0·14 p.p.m. (3·8 p.p.m. ±4 per cent.) and that of the group F samples is 3·1 ± 0·10 p.p.m. (3·1 p.p.m. ±3 per cent.).

A simplified treatment of the results in group F in which it is assumed without regression analysis that $Y = A_1X$ may be of interest.

Table III shows the results, in p.p.m., obtained in the group F experiments. Subtraction of the β-carotene added (column 2) from that found (column 3) gave an estimate (column 4) of that naturally present in the pea-flour. These results were found not to differ significantly (F- and *t*-tests) from the results (F_2 series) obtained with pea-flour to which carotene had not been added. The carotene that had been added was, therefore, completely recovered, and there was no loss in the process. It is readily calculated from the standard error that the accuracy of the mean (3·1 p.p.m. of carotene) is 3·1 ± 0·19 p.p.m. in 95 per cent. of cases.

This compares well with the result of the more elaborate analysis given above (3·1 ± 0·10 p.p.m.).

The simplified method applied to the group E series yielded for the accuracy of the mean at the 95 per cent. level, 3·8 ± 0·24 p.p.m. The results for group F were, as stated above, more satisfactory than the group E results.

TABLE III

SIMPLIFIED TREATMENT OF RESULTS

Set F_1				Set F_2	Comparison of Sets F_1 and F_2 (columns 4 and 5) Mean, Set F_1 = 3·11 " " F_2 = 3·04		
β-Carotene added to pea-flour samples		Total carotene found	Carotene naturally present	Carotene in untreated pea-flour	Variance ratio (F)	Probability %	Significance
μg.	p.p.m.	p.p.m.	p.p.m.	p.p.m.			
(1)	(2)	(3)	(4)	(5)			
12·8	3·2	6·4	3·2	3·0	1·69	>10	—
"	2·8	6·1	3·3	3·2			
"	3·2	6·3	3·1	3·3	value of t		
"	3·1	5·9	2·8	2·9	0·801	>10	—
"	2·7	5·7	3·0	2·9			
"	2·6	5·5	2·9	3·0	Standard Error of difference between means, S = 0·087		
"	2·9	6·2	3·3	2·9			
"	3·3	6·6	3·3	3·3			

STABILISATION OF CAROTENE

The fact that there is no significant loss of the carotene added in the experiments shown in Tables II and III indicates the presence in natural pea-flour of a substance that stabilises carotene during the removal of acetone by evaporation. It is possible that tocopherol, which occurs in peas, is the protective agent during the estimation of carotene by this method. Kozin and Bessonov[21] have shown that pea-flour contains an anti-oxidant which prevents rancidity in sunflower oil, though an ether extract is ineffective; Lieck and Willstaedt[23] have determined the amount of the anti-oxidant α-tocopherol in peas; tocopherols are known to be stabilisers for carotene.[9,39]

SUMMARY

A rapid two-stage chromatographic method applicable to the determination of total carotene (about 3 p.p.m.) in dried peas is described. The various stages in the analytical procedure were studied statistically in a series of control experiments involving the recovery of added β-carotene. In such recovery from pea-flour previously stripped of carotene, it was found that the greater portion of the pigment was lost in the stage involving removal of acetone from a carotene solution by evaporation. This loss was reduced when traces of an anti-oxidant (quinol) were added to the stripped pea-flour.

A statistical examination of the results of experiments in which β-carotene was added to untreated pea-flour showed that the method is efficient in that there was a linear relationship between the quantity of pea-flour taken and the quantity of natural carotene found.

The accuracy of the results at the 95 per cent. level for a 4·3 g. sample is better than ±5 per cent. of the carotene present.

The results also indicate that pea-flour contains a substance which stabilises carotene during removal of acetone by evaporation.

The thanks of the authors are due to Dr. V. H. Booth for advice, to Messrs. Lever Brothers and Unilever Limited (Dr. G. C. Hampson and Dr. R. F. Hunter) for gifts of β-carotene and to the Directors of Batchelor and Company (Ireland) Limited, for facilities afforded to one of us (F. B. L.).

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DEPARTMENTS OF CHEMISTRY AND MATHEMATICS
UNIVERSITY COLLEGE
DUBLIN

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Notes

AMPEROMETRIC TITRATION OF MERCAPTANS

It has recently been reported[1] that the strength (purity) of mercaptans determined by amperometric titration under the conditions given by Kolthoff[2] had given results several units less than 100 per cent., despite the fact that the total sulphur determination indicated that a pure material had been used. The authors attributed this to the fact that mercaptans easily oxidise to the disulphide (which would cause little change in the total sulphur content) and they inferred that the amperometric titration gives a correct measure of the mercaptan content.

Results obtained in these laboratories by amperometric titration on β-mercaptonaphthalene were lower than the results by iodine titration, and a short investigation was undertaken to ascertain whether or not amperometric titration produced results at the right level.

Two mercaptans, β-mercaptonaphthalene and mercaptobenzthiazole, were purified by recrystallisation, their purities were checked by alternative methods (see below) and they were then examined amperometrically by silver nitrate titration in ammoniacal ethanol solution. The results are given in Table I.

TABLE I

	β-Mercaptonaphthalene	Mercaptobenzthiazole
	%	%
Strength by titration with sodium hydroxide ..	—	99·6
Strength by titration with iodine	98·9	—
Strength by amperometric titration	95·0	97·5

It was suspected that the low amperometric results were due to oxidation occurring during the course of the titration, and this was confirmed by stirring an ammoniacal ethanol solution of β-mercaptonaphthalene in air for ½ hr. before titration with silver nitrate; a result of 60·7 per cent. was obtained.

Further tests were carried out in order to ascertain the source of the oxidising agent; the results, together with values obtained by iodine titration, sodium hydroxide titration and potentiometric titration[3] (using aqueous silver nitrate instead of alcoholic silver nitrate) are given in Table II. In test (*a*) the β-mercaptonaphthalene solution was prepared and titrated under an atmosphere of nitrogen, and the result (compare with Table I) shows that in a normal titration atmospheric oxidation is a negligible factor; an aliquot portion from the initial β-mercaptonaphthalene solution was also titrated with 0·01 *N* iodine solution, with a result 98·6 per cent., from which it is concluded that no oxidation occurs on standing in *neutral* alcohol solution.

In test (*b*), the solution was stirred under nitrogen for ½ hr., the mercaptan was titrated and then a second aliquot portion of mercaptan solution was added and titrated. It was hoped that any oxidising agent in the ammoniacal ethanol would be used up in oxidising the first portion of mercaptan, and that the second portion of mercaptan would not be subject to oxidation from this cause. The titres on the first and second portions corresponded to purity figures of 82 and 94·4 per cent. respectively; the difference must be due to slow oxidation (during the first test) caused by an oxidising agent in the ammoniacal ethanol.

TABLE II

Strength by	β-Mercaptonaphthalene	Mercaptobenzthiazole
	%	%
Iodine titration	98·9	—
Sodium hydroxide titration	—	99·6
Potentiometric titration[3]	98·9	—
Amperometric titration:		
(*a*) Under nitrogen (immediate titration) ..	95·2	98·8
(*b*) Under nitrogen:		
(i) After ½ hr. stirring	82	—
(ii) Second portion of mercaptan solution added after completion of (*b*) (i) ..	94·4	—
(*c*) As in (*a*) with silver nitrate in boiled-out distilled water	97·3	—

Test (*c*) was carried out under nitrogen, using silver nitrate that had been freshly prepared with boiled-out distilled water. The result is substantially higher than in the other amperometric tests, and is not very far short of the iodine figure and potentiometric titration figure. It is concluded that the main sources of oxidising agent are the dissolved air in silver nitrate solution

as normally used and the ammoniacal ethanol. It will be noted that the potentiometric titration in neutral alcohol solution gives a satisfactory result, as the mercaptan is less susceptible to oxidation in neutral than in ammoniacal solution. It might be possible to develop an amperometric titration in neutral alcohol solution, but there would appear to be no advantage in doing this.

In the case of mercaptobenzthiazole, agreement between the alkali titration and amperometric titration methods is rather better, presumably owing to the greater stability of the mercaptan group in mercaptobenzthiazole.

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N. STRAFFORD
F. R. CROPPER
A. HAMER

ANALYTICAL LABORATORIES
IMPERIAL CHEMICAL INDUSTRIES LTD.
BLACKLEY, MANCHESTER, 9

May, 1949

THE FRUCTOSE UREA AND FRUCTOSE ACETONE REACTIONS AS SELECTIVE TESTS FOR SUGARS

As is well known, urea combines with furfural in concentrated acids to form an unstable violet pigment (Schiff[1]). With ω-hydroxymethyl furfural, and its reduction product "methyl-furil," the pigment is bright blue (Fenton[2]). The furfural reaction has been used by Nakashima and Maruaka[3] for estimation of urea in blood plasma, stannous chloride being added to protect the aldehyde from decomposition during the condensation. A converse form of the reaction has been introduced by Foulger[4] as a test for keto-hexoses; he uses as the reagent a 40 per cent. solution of urea in 40 per cent. sulphuric acid containing 2 per cent. of stannous chloride. The value of the reducing agent when urea is used as a sugar reagent is doubtful, since it can be shown that mild oxidation is necessary for final development of the colours in all the sugar reactions depending on formation of a furfural as intermediate. By omitting the stannous chloride and substituting hydrochloric for sulphuric acid, the fructose urea reaction can be applied as a simple and very delicate selective test for keto-hexoses.

METHOD—To about 0·5 to 1 g. of urea in a dry porcelain dish add 5 or 6 drops of concentrated hydrochloric acid and 2 or 3 drops, not more, of the sugar solution. Gently shake until the urea has dissolved. Heat on a boiling water-bath. If the sugar solution contains fructose in concentrations of 0·5 to 1 per cent., a bright, turquoise-blue ring will appear within 5 minutes, and eventually close in to form a small pool of blue syrup. More dilute solutions require longer times, but the test will reveal fructose in 2 drops of a 0·01 per cent. solution within about 15 minutes. The test is very sensitive, and the lower limit is of the order of 5 μg. of fructose, or 15 μg. of sucrose. Of course, greater delicacy can be obtained by concentrating some of the fructose solution with the urea prior to adding the acid. Excess of urea is necessary to stabilise the pigment in the final viscid mixture. Water de-sensitises the reaction. If sulphuric acid or hydrobromic acid is used instead of hydrochloric, the pigment will be destroyed.

SELECTIVITY—The blue reaction is characteristic of keto-hexoses, including fructosides, sucrose and inulin, and sorbose. Non-ketose sugars only react chromatically when in relatively high concentration and after longer times. Aldo-pentoses and pentosans give yellow colours; aldo-hexoses and hexosans give red or red-purple colours. Crystalline ascorbic acid does not react, apart from the faint blue due to contamination with sorbose. Even in presence of foreign sugars, the fructose reaction can be recognised by the early appearance of the characteristic blue ring. For exact work it is necessary to extract the pigments with ethanol, and spectrograph the mixture. As obtained in the spot test, the blue pigment is insoluble in chloroform but freely soluble in acidified alcohols and in dilute acids. It is reversibly changed to red by alkalis. When the solution in ethanol is concentrated the pigment separates out as an amorphous, indigo-like precipitate, but has not yet been obtained in crystalline form.

Urea cannot be replaced by ammonium salts, acetamide, glycine, ethyl carbamate, methylamine, methylurea or thiourea. Guanidine salts, as Foulger has observed, give red-purple colours with aldo-hexoses as well as with fructose. Out of a variety of non-nitrogenous compounds tested, acetone was found to be the only one that reacted in a manner somewhat similar to urea in the

sugar tests. Owing to its volatility it cannot be used in the spot test, and, generally, it is less sensitive and less selective as a fructose reagent. As the colour reaction between acetone and the sugars does not appear to have attracted attention, it is briefly described here as a qualitative test.

The acetone test

Method—Mix 4 or 5 drops of acetone with 5 ml. of concentrated hydrochloric acid. Boil vigorously for a few seconds, not long enough to expel the acetone. Add 1 or 2 drops, not more, of the sugar solution. Mix and allow the mixture to cool spontaneously. With fructose solutions down to 1 per cent., a violet colour, changing to blue, soon develops. Concentrations down to 0·1 per cent., which is about the lower limit of the test, require 10 minutes for colour development. The test is positive with a "pin-head" (0·5 mg.) of solid fructose. Even a slight excess of water must be avoided, as it completely inhibits the test. Non-ketose sugars do not react appreciably in original concentrations below 1 per cent.; above this, they produce colours ranging from red to purple, some of which resemble those due to fructose.

This work forms part of an investigation into the composition of marine algae, carried out by the aid of a grant from the Medical Research Council of Ireland.

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William R. Fearon
J. A. Drum
Department of Biochemistry
Trinity College, Dublin

April, 1949

Official Appointments

Mr. Noel L. Allport, F.R.I.C., has been appointed Analyst (Drug Testing) to the Ministry of Health, and Analyst to the Port of London Authority.

PUBLIC ANALYST APPOINTMENTS

Notification of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1949, **74**, 604).

Public Analyst	*Appointments*
Alcock, Arthur	Boroughs of Eccles and Stretford.
Davson, Archibald Prideaux (Deputy)	Metropolitan Borough of Greenwich.
Hamence, Jack Hubert	Urban District of Hornchurch.
Taylor, George	Urban District of Hornchurch.
Williams, Hugh Amphlett	Metropolitan Borough of Greenwich.

Reviews

Biochemical Preparations. Volume I. Edited by H. E. Carter. Pp. xi + 76. New York: Wiley & Sons Inc. London: Chapman & Hall, Ltd. 1949. Price 15s.

To those who have used *Organic Syntheses*, this first volume of *Biochemical Preparations* will have a familiar appearance, for both series are closely similar in style and format. It is intended that this book, which will be followed by other volumes at intervals of twelve to eighteen months, will do for biochemistry what *Organic Syntheses* did for organic chemistry. Very wisely the editors, before launching the new series, conferred with the editors of *Organic Syntheses*, so that they have been able to profit by the experience gained in the publication of the older series. The new volumes will certainly meet a long-felt need; they will describe, with full details, methods of preparing compounds of natural origin not readily available commercially. This is an even more difficult task than that which confronted the editors of *Organic Syntheses* in view of the greater number of variables involved and the difficulty of putting into words the subtle differences of technique that sometimes make for success or failure in biochemical work. It will be interesting to see to what extent the yields and purities claimed in this volume can be reproduced by workers in different laboratories, even though each preparation submitted is invariably checked in an independent laboratory before publication.

Although the format of *Organic Syntheses* has been closely followed there is one important difference; in *Biochemical Preparations* an additional section (Properties and Purity of Product) has been included for each substance. This information is most helpful, as it is generally more difficult to lay down standards of purity for substances made from natural sources than for synthetic compounds, and in any event, it is frequently more important to know what impurities are present than to be assured that a substance is almost pure.

The preparations listed in this volume comprise: adenosine di- and tri-phosphate, diphosphopyridine nucleotide, the α-glucose-1-phosphates and DL-glyceraldehyde-3-phosphoric acid; L-alanine, L-serine (together with three of the reagents required for making these two amino acids), β-3 : 4-dihydroxyphenyl-L-alanine, L-glutamine, L-lysine monohydrochloride and D-tyrosine; casein, lycopene and lysozyme.

The book also contains a list of the compounds of biochemical interest which have appeared in *Organic Syntheses*, but the reviewer was somewhat puzzled to see in this list "Casein," the preparation of which is actually described in this first volume of *Biochemical Preparations*. This seems an instance of unnecessary duplication, but the two methods differ significantly in details and presumably the newer method offers some advantages over the earlier one; one would surely have expected a word of explanation, but the method described in *Organic Syntheses* is not even referred to.

There is no doubt about the success the new series will have, and the volumes will become as indispensable in the biochemical laboratory as *Organic Syntheses* has become in the organic laboratory.

The book is well printed and the binding is sufficiently substantial to withstand the constant usage that a book of this type will undoubtedly receive. Biochemists will look forward with interest to the subsequent volumes promised. F. A. ROBINSON

CANNING TECHNOLOGY. By A. J. HOWARD, M.A., A.R.I.C. Pp. viii + 287. London: J. & A. Churchill, Ltd. 1949. Price 30s. net.

Twenty years ago most sections of the canning industry in this country were in their infancy. The intervening years have been ones of rapid growth, education and discipline, with the result that the industry is now not only of considerable size, but is well instructed in the scientific principles on which it is based, and fully aware of the responsibility it must bear in matters of public health. In its early period of growth the principal textbooks available were written chiefly for the practical canner and, while dealing comprehensively with the operations required for each particular product, tended to ignore, or to give scant attention to, the fundamental principles of the preservation of food by heat. The works chemist was left to rummage through the scientific and technical journals if he wished to equip himself with adequate knowledge of his subject.

The situation improved considerably with the publication, six years ago, of a small but excellent book on the microbiology of canning, but this work was necessarily limited in its scope, and a fuller survey of the scientific aspects of canning was still required. The book now under review meets this need, and is written with the authority of one who held for a time the office of Director of Canning at the Ministry of Food.

After a short historical introduction the author devotes three chapters—more than one-third of the whole book—to consideration of the tinplate container. This emphasis on the can—its origin, structure and behaviour—is welcome, as the importance of the container is apt to be overshadowed by other factors more obviously concerned with the quality and purity of the contents. These three chapters deal with the modern methods of manufacture of tinplate, the fabrication and lacquering of cans and the types of internal and external corrosion that may develop when the cans are stored. The section concerned with the electrochemistry of corrosion is particularly clear and comprehensive. Attention is next given to problems encountered in establishing a cannery, to the methods used in examining and preparing the raw food materials, and to the operations of exhausting, closing and processing. Excellent illustrations and descriptions of modern canning equipment make it possible to follow the operations in detail, and the balance between the scientific and technological aspects of each subject is well observed. Other chapters deal with the principles of heat sterilisation, the causes and prevention of microbiological spoilage, and the metallic contamination of canned foods.

It is in the chapter dealing with the principles of heat sterilisation that the reader may possibly find himself least convinced by the arguments put forward, though it must be added that these are strictly orthodox. The author stresses the view that the survival of bacterial spores is largely determined by their individual heat resistance, and that there is some point in the heat process

at which complete destruction of the spores can be guaranteed. The newer alternative hypothesis, that every spore has a finite chance of survival, however severe the process may be, and that processing times are related to the initial infection and to the degree of survival that can be tolerated for each type of spore, might have been mentioned with advantage.

In future editions, which will no doubt be called for, rather more space might be devoted to the health aspects, including nutritional values, of canned foods. As it is there is little doubt that scientists and canning technologists will benefit by careful study of this book. It is pleasant to read, not only on account of the agreeable style in which it is written, but also for its attractive lay-out and printing, and for the large number of clear illustrations and diagrams with which it is provided. W. B. ADAM

ABSORPTION SPECTROPHOTOMETRY. By G. F. LOTHIAN, M.A., F.Inst.P. Pp. 196. London: Hilger & Watts, Ltd. 1949. Price 26s. net (plus postage 9d.).

This book is a successor to Twyman and Allsopp's *The Practice of Absorption Spectrophotometry* (Second Edition, 1934). Considerable developments have taken place since 1934 in the techniques of photo-electric spectrophotometry in the visible and ultra regions and in equipment for infra-red spectroscopy. An increasing number of important analytical problems have been or are being solved by methods which culminate in measurements of light absorption, and the photo-electric absorptiometer is replacing visual colorimetry just as photo-electric spectrophotometry is taking the place of photographic methods. For many purposes, however, some of the older methods are far from being obsolete and a great deal of useful work can still be done with sector photometers, quartz spectrographs and visual spectrophotometers, instruments that cost little to maintain and do not deteriorate. For other purposes, photo-electric spectrophotometry, more sensitive to small differences in absorption intensity, is indispensable. There are further problems which though not open to attack by the methods based on selective absorption of visible or ultra-violet rays, are readily solved by the methods of infra-red spectroscopy. In this field the older equipment is obsolete. The newer techniques are accurate and speedy and there is a growing body of fact and interpretation which progressively assists application to new problems.

Many of the best instruments are American; supply has stimulated demand and demand production. In this country instrument manufacturers have been through a difficult time since 1939, and the dollar "famine" adds urgency to the hope that their great efforts to meet the needs and even outstrip their competitors will soon be successful.

Mr. Lothian's book is in three parts: (1) Principles of Spectrophotometry, (2) Applications and (3) Technique. Chapter V on methods of calculation in the application of spectrophotometry to quantitative analysis will be found particularly useful. Chapter XII on infra-red techniques, although excellent in its way, is inadequate, and the subject-matter perhaps needs more space in later editions.

All users of spectroscopes will find much that is of value to them in this book. R. A. MORTON

THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Founded 1874 Incorporated 1907

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry by holding periodical meetings, by promoting lectures, discussions and conferences, and by the publication of a journal devoted to analytical chemistry; to study questions relating to the adulteration of food, drugs and commercial articles generally, and its detection; and to promote the efficiency and proper administration of the laws concerned with the repression of adulteration.

Every candidate for membership of the Society must be not less than twenty-one years of age and be or have been engaged in analytical, consulting or professional chemistry. Each candidate for election must be proposed by three members of the Society, who must provide written testimony of their personal knowledge of his or her scientific and professional fitness. If the council of the Society in their discretion think fit such testimony may be dispensed with for a candidate not residing in the United Kingdom. Every application is placed before the council and the council have the power in their absolute discretion to suspend or reject any application, or to elect the candidate to membership.

The Entrance Fee is £1 1s. The Annual Subscription is £2 2s. The Society's official year runs from March to March, but the financial year begins on January 1st and subscriptions are due on that date.

Ordinary Meetings of the Society are held in London, usually on the first Wednesday in October, November, December, February, April and May; the Annual General Meeting is usually held on the first Friday in March. Notices of all meetings are sent to members by post.

THE ANALYST, the official organ of the Society, is issued monthly to members, and contains reports of the proceedings of the Society, original papers and notes, information about analytical methods, Government reports, and reviews of books. All members receive in addition *Abstracts C*, the analytical section of British Abstracts, providing a reliable index to the analytical literature of the world.

Forms of application for membership may be obtained from the Secretary, 7-8 Idol Lane, London, E.C.3.

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THE North of England Section and the Scottish Section were formed to promote the aims and interests of the Society among members in those areas. Members residing in England or Wales north of Birmingham may become members of the North of England Section, and those residing in Scotland members of the Scottish Section.

The Microchemistry Group, the Physical Methods Group and the Biological Methods Group have been formed within the Society to further the study of the application of microchemical, physical and biological methods of analysis. All members of the Society are eligible for membership of the Groups.

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The Sections and Groups hold their own meetings from time to time in different places.

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REQUIRED by the Government of Southern Rhodesia, a male Assistant Analytical Chemist for appointment in the Government Analyst's Laboratory in Salisbury, Southern Rhodesia. Professional qualification must be of specialised honours degree or A.R.I.C. standard.

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Application forms and further information may be obtained from the Secretary to the High Commissioner for Southern Rhodesia, 429, Strand, London, W.C.2, to whom completed forms should be returned not later than 25th February, 1950. Canvassing will disqualify applicants.

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CONTENTS

Editorial *Page*

"The Analyst" for 1950 .. 1

Proceedings of the Society of Public Analysts and Other Analytical Chemists

Joint Meeting of the Society with the Food Group of the Society of Chemical Industry on December 6th, 1949 .. 2

New Members .. 2

Original Papers

The Determination of Chromium in Chromite

Part I. Volumetric Determination of Chromate with Special Reference to the Effects of Vanadate and Arsenate—W. Furness .. 2

Part II. Determination of Chromium in a Synthetic Sample of Known Composition—P. J. Hardwick .. 9

Part III. Determination of Chromium in a Standard Sample of U.S. National Bureau of Standards Chrome Refractory No. 103 by Selected Methods—F. J. Bryant and P. J. Hardwick .. 12

Extraction and Photometric Estimation of Some Metals with 8-Hydroxyquinoline—C. H. R. Gentry and L. G. Sherrington .. 17

A Method for the Dry Assay of Sulphides and Oxides of Lead and Bismuth—J. A. Smythe .. 21

The Determination of Small Quantities of Copper in Lead and Lead Alloys—P. L. Willmott and F. J. Raymond .. 24

Gravimetric Determination of Copper, Iron, Aluminium and Titanium with N-Benzoylphenylhydroxylamine—Sudhir Chandra Shome .. 27

Application of Radio-Frequencies to Conductimetric Analysis (Rectified Radio-Frequency Method)—G. G. Blake .. 32

Some Applications of a Modified Technique in Paper Chromatography—L. Rutter .. 37

Investigations in the Examination and on Variations in the Composition of Milk. Part I. The Determination of the Hortvet Freezing-Point—R. W. Sutton, J. Markland, A. Barraclough and W. B. Chapman .. 42

The Determination of Carotene in Dried Peas David Franklin, F. B. Lyons and T. S. Wheeler .. 49

Notes

Amperometric Titration of Mercaptans—N. Strafford, F. R. Cropper and A. Hamer .. 55

The Fructose Urea and Fructose Acetone Reactions as Selective Tests for Sugars—William R. Fearon and J. A. Drum .. 56

Official Appointments .. 57

Reviews

Biochemical Preparations, by H. E. Carter .. 57

Canning Technology, by A. J. Howard .. 58

Absorption Spectrophotometry, by G. F. Lothian .. 59

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