

THE ANALYST

A Monthly Publication
dealing with all branches
of Analytical Chemistry:
the Journal of the Society
of Public Analysts and
Other Analytical Chemists



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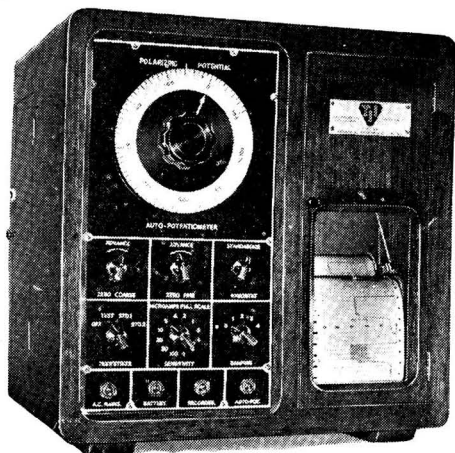
Volume 75

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No. 894, Pages 453-508

September 1950



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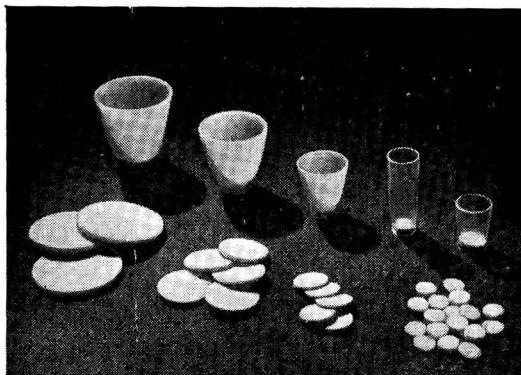
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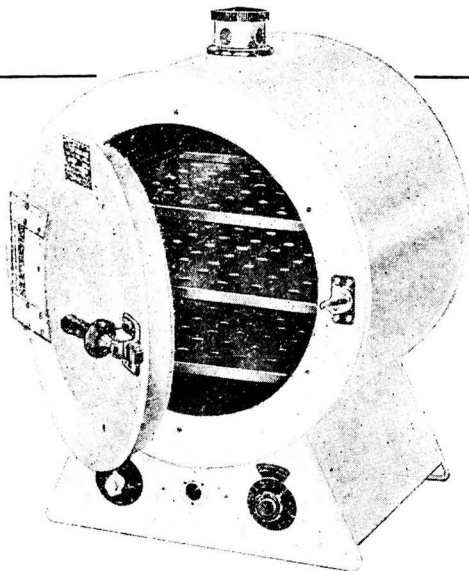
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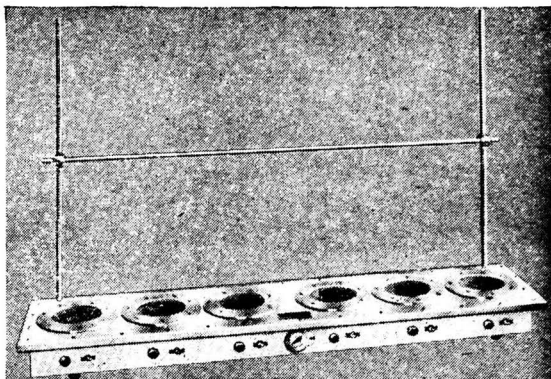
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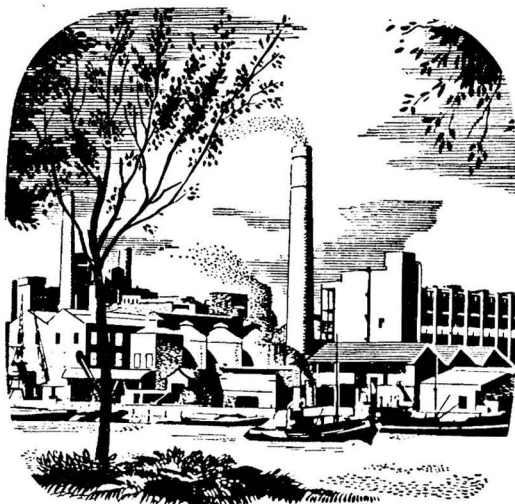
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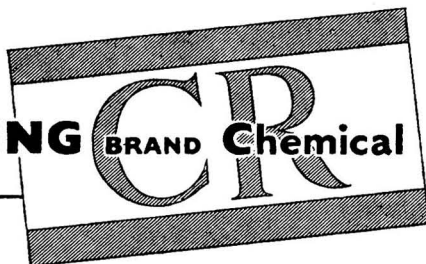
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PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

BIOLOGICAL METHODS GROUP

A MEETING of the Group was held at 2.15 p.m. on Tuesday, May 23rd, 1950, at the Medical Society of London, Chandos Street, Cavendish Square, London, W.1. The chair was taken by Dr. S. K. Kon. About one hundred members and guests were present.

The subject of the meeting was "The Assay of Vitamin B₁₂"; after an introduction by the Chairman, the following papers were read and discussed: "Assays of Vitamin B₁₂ in Man," by C. C. Ungley; "Chick Assays," by Miss M. E. Coates; "The Cup-Plate Assay of Vitamin B₁₂," by W. F. J. Cuthbertson, J. T. Lloyd and H. F. Pegler; "Some Observations on the Cup-Plate Assay for Vitamin B₁₂ using *Lactobacillus lactis* Dorner 10697," by Frances E. Larkin and R. E. Stuckey; "The Assay of Vitamin B₁₂ by the Turbidimetric Method using *Lactobacillus leichmannii* 313," by W. B. Emery, K. A. Lees and J. P. R. Tootill; "A Comparison of *Lactobacillus lactis* Dorner and *Lactobacillus leichmannii* for the Assay of Vitamin B₁₂ by a Test Tube Method," by G. E. Shaw; "Experience with the Microbiological Assay of Vitamin B₁₂ in an Analytical and Consulting Laboratory," by H. Pritchard.

PHYSICAL METHODS GROUP

THE twenty-sixth Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, May 23rd, 1950, in the Meeting Rooms of the Iron and Steel Institute, London. Mr. B. S. Cooper, the Chairman of the Group, was in the chair and about forty members and visitors were present.

The following papers on Radio Chemistry in Analytical Chemistry were read and discussed: "Radiometric Assay in Tracer Research," by F. P. W. Winteringham, A.R.I.C.; "The Determination of Potash (in Fertiliser) by Measurement of its Radioactivity," by D. S. Lees, B.A., A.Inst.P., W. Broomfield and H. N. Wilson, F.R.I.C.; "Radioactivation Analysis—Some Glimpses of its Scope," by A. A. Smales, B.Sc.

DEATHS

WE regret to record the deaths of

Eric Cecil Keeley
Theodore Rendle.

The Chromatographic Determination of Raffinose in Raw Sugars

BY N. ALBON AND D. GROSS

SYNOPSIS—A paper chromatographic method is described for the separation of raffinose from other sugars in a mixture. The raffinose is made visible by spraying with a suitable reagent. A quantitative estimation is possible by visual comparison of the developed spot with standard spots produced by known quantities of pure raffinose. This technique is sufficiently sensitive to yield a positive result with as little as 0.05 per cent. The method has been applied to the determination of raffinose in a large number of raw beet sugars.

EXISTING procedures for the determination of raffinose in sugar products are based mainly on the principle of the Clerget inversion or double polarisation method. Of these methods the two-enzyme procedure of Paine and Balch¹ is the most accurate and reliable, but the high cost of the enzymes, the skill and time required for this method make its adoption for routine use difficult. Owing to the limitations of the optical methods, especially when applied to technical products, the accuracy to be expected is not very high. According to Browne and Zerban² the indication of a smaller amount of raffinose than 0.5 per cent. in commercial products is extremely doubtful.

The object of the present investigation has been to devise a more rapid and accurate method for determining raffinose in commercial sugar products such as raw beet sugars.

Partridge³ has shown the possibility of separating very small quantities of sugars by the use of paper chromatography. Preliminary experiments with known synthetic mixtures of sucrose and raffinose soon demonstrated the advantages of this method. The high sensitivity of the technique is a great advantage when dealing with products containing very small amounts of raffinose, mostly below 0.5 per cent., for which available methods are not suitable. A method has been developed which can be employed for the routine analysis of sugar products, particularly raw sugars, and which compares favourably with the available methods, both as regards accuracy and sensitivity. The paper chromatographic technique employed enables a large number of samples to be analysed simultaneously and the method is sufficiently rapid, simple and inexpensive to be adopted for routine use. The possibilities of this method were pointed out by H. C. S. de Whalley.⁴

METHOD

Apparatus—All-glass tanks were used for most of the experiments. Accumulator vessels were modified for this purpose. Tanks of dimensions up to 9 × 32 × 30 inches were used according to number and size of chromatograms run. To minimise temperature changes, the tanks were lagged with several layers of cotton wool or other insulating material. The troughs holding the solvents were made from Pyrex glass or Polythene tubing of approximately one and a quarter inches outer diameter. The troughs were supported inside the tanks by suitably cut strips of glass. The drying cabinet was 6½ × 26 × 30 inches, with a glass window 16 × 16 inches. Air, drawn in at the bottom over heating elements by means of a fan, flowed round the suspended chromatogram and was discharged from the top into a fume cupboard. The heating and air flow could be varied. Reagents were applied from glass spraying bottles connected to an air compressor so as to obtain an even and strong spray.

REAGENTS—

Whatman's No. 1 paper of size 18¼ × 22½ inches or 24 × 24 inches was used. The following solvent mixture was used—

<i>n</i> -Butanol, lab. reagent	5 parts by volume
Pyridine (A.R.)	3 "
Water	3 "
Benzene, lab. reagent	1 "

Mix gently in a separating funnel and allow to stand until the upper layer is transparent. Use the upper layer as solvent in the trough, and the bottom layer for saturation of the atmosphere in the tank.

Spraying reagent—Make up a 1 per cent. (w/v) solution of α -naphthol (A.R.) in ethanol and filter. Before use, mix 50 ml. with 5 ml. of phosphoric acid (A.R.).

PROCEDURE

Make up a 40 per cent. (w/v) solution of the raw sugar sample and prepare standards from a raffinose-free raw sugar solution (40 per cent. w/v) and pure raffinose hydrate (Kerfoot's Biochemical Reagent). Draw a pencil line parallel to, and 12 cm. from, the top of the paper sheet (Whatman's No. 1) and mark the points of application for each sample and standard 3 cm. apart. Apply from a micro-pipette 5 μ l. of each solution to the appropriate mark. Allow a few minutes for drying and repeat the application, making a total amount of 10 μ l. (4 mg. of sugar). Leave to dry for 30 minutes, fold the top of the sheet around a glass strip, 3 cm. wide, and place it in the trough containing the solvent. After 24 hours at room temperature (15° to 25° C.), remove the chromatogram from the tank avoiding the spillage of surplus solvent down the sheet. Shorter runs of 16 hours often give sufficiently good separations. Hang in the drying cabinet and remove the solvent in a stream of air at 90° C. for 1 hour. Transfer to a fume cupboard and spray both sides rapidly and evenly with the α -naphthol reagent. The quantity of reagent required is approximately 1 ml. per 25 sq. cm. At no time during the spraying should the reagent be excessive or be allowed to flow over the surface of the paper. Replace the chromatogram in the drying cabinet and heat for 10 minutes at 90° C. to allow the colour of the spots to develop. Remove and immediately compare, by transmitted light, the raffinose spots in the samples with those in the standards.

General remarks on the method—The method has proved to be applicable to a fairly wide range of sugar products, although it was primarily employed for the analysis of raw sugars. A preliminary run will indicate the approximate concentration of raffinose present and the standards required. With samples containing more than 0.4 per cent. of raffinose the quantity taken for the chromatogram may conveniently be reduced to 2 mg. (5 μ l. of solution). This decreases the possible interference by salts in high concentration, such as are present in sugars with more than 1.5 per cent. of ash. These sugars can readily be de-ionised by passage through mixed beds of ion exchange resins prior to their application to the chromatogram. Examination of a large number of raw beet sugars showed that raffinose was always present, but none was detectable in a number of raw cane sugars. The standards were therefore prepared from a raw cane sugar in preference to a synthetic mixture of pure sugars.

The chromatograms can conveniently be copied by exposing reflex copying paper through the chromatogram, with a yellow filter over the light source. Given even lighting and correct exposure, these copies may be used for the estimation of the raffinose. As the spots fade, copies should be made within half an hour.

RESULTS

Many samples of raw beet sugars have been examined by the method described above. The results are summarised below in Tables I and II.

Table I shows the accuracy of visual comparison of the separated raffinose spots with standards. The standards were made up in steps of 0.1 per cent. and intermediate concentrations could be estimated to an accuracy of 0.05 per cent. The figures represent the differences between the estimations by two analysts from the same chromatograms. Each sample was run singly, not in duplicate. Estimations were made from the original chromatogram and also from the photographic copy.

TABLE I
ESTIMATIONS OF A SERIES OF SAMPLES BY TWO ANALYSTS

Difference in estimation, %	Original chromatograms	Photographic copies
0.2	2	1
0.15	13	2
0.1	33	40
0.05	129	132
nil	175	170
	Total 352	Total 345

Table II shows the results obtained by running chromatograms of five samples at various times and under various conditions. Standards were made up from different raw sugars; tanks of various dimensions were used, the paper sheets were from different batches and of various sizes, and the solvents were mixed separately for each run. The room temperature varied within 10° C. Estimations were made from the original chromatograms by four analysts and the mean figures taken except in determination No. 1.

TABLE II
ESTIMATIONS OF FIVE SAMPLES, UNDER VARIOUS CONDITIONS, BY FOUR ANALYSTS
Raffinose content, per cent.

Sample	Determination					Maximum difference
	No. 1	No. 2	No. 3	No. 4	No. 5	
A	0.10	0.10	0.11	0.07	0.10	0.04
B	0.20	0.28	0.29	0.26	0.21	0.09
C	0.30	0.38	0.36	0.39	0.37	0.09
D	0.40	0.41	0.45	0.44	0.40	0.05
E	0.40	0.32	0.36	0.35	0.37	0.08

DISCUSSION

Raffinose is known to occur generally in beet sugar products, but accurate determination of the amounts present is difficult by hitherto available methods and is liable to interference from other constituents. The chromatographic method permits the raffinose to be separated from the other sugars present and enables the identity of this sugar, free from interfering substances, to be confirmed in various ways.

The R_F value* of the raffinose in beet raw sugars is the same as that of pure raffinose under the same conditions and differs from the R_F values of any other sugar to our knowledge. In a number of different solvent mixtures, some of which were used for two-dimensional separations, the raffinose spot from the raw sugar behaved in the same manner as pure raffinose. The spraying reagent used reacts only with sugars yielding fructose on hydrolysis.

A number of equal volumes of a raw sugar solution were chromatographed together on a paper sheet and the spots corresponding to raffinose extracted. After concentration and precipitation with acetone, characteristic needle-shaped crystals were obtained, indistinguishable from those precipitated from pure raffinose.

In other experiments a number of the spots separated from the raw beet sugar were extracted and concentrated to give a 2 per cent. solution of the supposed raffinose. On inversion with invertase (Wallerstein's) this gave fructose and melibiose, and, on inversion with invertase containing melibiase (Wallerstein's), it yielded fructose, glucose and galactose. The presence of these sugars in the expected yields was demonstrated chromatographically, and so was the complete inversion of the supposed raffinose.

A limit to the sensitivity of the method is set by the minimum quantity of raffinose that can be detected by the spray reagent and the maximum load that can be applied to the paper sheet. The α -naphthol reagent compares favourably with other spraying reagents tested in respect of sensitivity, 2 μ g. of raffinose being detectable. Although other solvent mixtures that were tried gave good separations of the sugars, it was found that the mixture recommended has the best combination of high load, good separation and sharpness of spots for this particular application. An important feature of the method is that it enables a large number of samples to be examined at the same time. Thirteen samples and six standards can be analysed on one sheet of paper (24 \times 24 inches) and several such sheets can be placed in one tank.

$$*R_F = \frac{\text{movement of spot (band)}}{\text{movement of advancing front of liquid}}$$

The R_F value is characteristic of each compound in a given solvent under standard conditions and can be used for the identification of compounds.

This procedure has made possible the routine determination of raffinose in hundreds of samples within a short time and with comparative ease. In view of the small quantity of material required and the good agreement of results, the method has also proved of great convenience in exploratory and control work.

We wish to thank Mr. H. C. S. de Whalley, Director of Research, for valuable advice during the prosecution of this work, and the Directors of Tate & Lyle Limited for permission to publish this paper.

REFERENCES

1. Paine, H. S., and Balch, R. T., *Ind. Eng. Chem.*, 1925, **17**, 240; *J. Amer. Chem. Soc.*, 1927, **49**, 1019.
2. Browne, C. A., and Zerban, F. W., "Physical and Chemical Methods of Sugar Analysis," 3rd Ed., New York, 1941, p. 470.
3. Partridge, S. M., *Biochem. J.*, 1948, **42**, 238.
4. de Whalley, H. C. S., *Int. Sug. J.*, 1950, **52**, 127.

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Determination of Theobromine in Cocoa Products

BY K. E. HOLMES

SYNOPSIS—The existing methods for determining theobromine in cocoa and its products are described and a new and improved procedure is proposed. In this, the alkaloid is completely extracted by means of boiling water and magnesia, clarified with lead acetate, filtered, concentrated and extracted with chloroform.

The alkaloidal residue from the chloroform extract is then assayed by Boie's method. By this procedure the results are equal to, and sometimes higher than those by Wadsworth's method.

A rapid continuous extractor, for use with chloroform, is described.

THE determination of theobromine in cocoa products has always been difficult, and it has received considerable attention in recent years. The methods recently devised can be grouped under two headings.

- (a) Those using tetrachloroethane or chloroform after triturating with magnesia and a limited amount of water.
- (b) Those using aqueous solvent with added acid or alkali.

The methods in group (a), which are the best known, were initiated by Wadsworth,¹ whose method was modified by Macdonald,² Humphries,³ Kay and Haywood⁴ and Lowe.⁵ All these methods suffer from the defect that the amount of water to be left in the mixture of cocoa material and magnesia before the solvent is added is very critical. Insufficient water gives low results, too much yields an impure product, and there is always a doubt as to whether the extraction is complete or not.

The following is a résumé of recent work in the second group. Jalade⁶ steeped cocoa in dilute caustic soda, and Pritzker and Jungkunz⁷ heated it under a reflux condenser with water and magnesia. Both took an aliquot part of the clean extract and extracted it with chloroform in a continuous extractor. Martin and Clergue⁸ refluxed cocoa with 10 per cent. acid and continuously extracted the mixture with chloroform. Moir and Hinks⁹ extracted the alkaloid with aqueous ethanol and magnesia, evaporated the filtered extract to remove ethanol, extracted the clarified and filtered extract with successive amounts of chloroform, and assayed the final product by Kjeldahl's method. Parkes and Parkes¹⁰ used a mixture of chloroform and phenol instead of pure chloroform. Moores and Campbell¹¹ eluted cocoa material with boiling water, adsorbed the theobromine from an aliquot part of the clarified extract on a chromatographic column, eluted with alkali and estimated the alkaloid by electrometric titration.

Of these methods, those of Jalade and of Moir and Hinks are rather lengthy. In the author's experience, that of Pritzker and Jungkunz gives low results, and the same may be said of the method of Martin and Clergue. The Moores and Campbell method is laborious; it uses rather small quantities of sample and the extraction of theobromine is incomplete.

EXPERIMENTAL

In the present research a method was devised which obviated some of the faults of those mentioned above. Complete extraction of theobromine was effected, with reduced manipulation, in a working day of 8 to 10 hours. In this work the Wadsworth¹ method was used for the sake of comparison, and the Boie¹² method for assaying the extracted theobromine.

Despite the high solubility of theobromine in tetrachloroethane, this solvent was avoided and water was used instead. It was shown firstly that all the alkaloid could be extracted from cocoa material of known theobromine content by refluxing 10 g., together with 5 g.

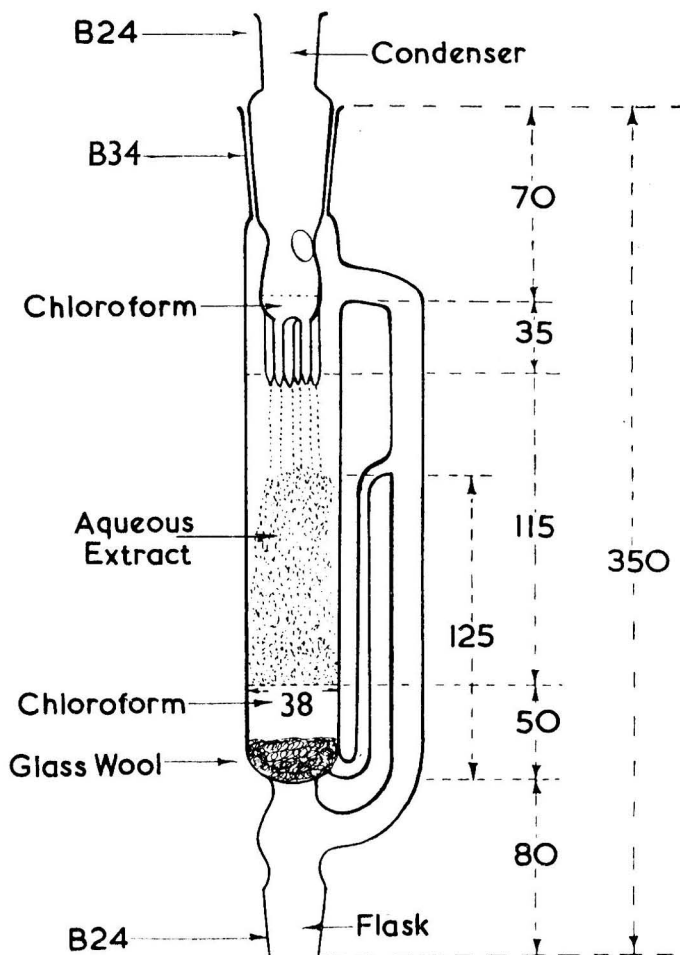


Fig. 1. Rapid liquid - liquid extractor. Dimensions in millimetres.

of magnesium oxide, three times with 250-ml. portions of water, followed by filtration and evaporation to dryness. The dried residue, when extracted with more magnesia and tetrachloroethane by the Wadsworth method, gave a quantitative yield. It was found that if the mixture of cocoa, magnesia and water was clarified, better filtration resulted and that the impurities in the extract were reduced. For this purpose, basic lead acetate solution was found suitable and no loss was observed as a result of its use. An aliquot part of the filtrate was taken after only one extraction, but this led consistently to low results. The loss was

traced to the adsorption of alkaloid by magnesia, for when pure theobromine alone was carried through the aliquot part process, not more than 95 per cent. could be recovered. Complete washing, on the other hand, gave a quantitative yield.

Having got all the theobromine into aqueous solution, the next problem was how best to isolate it. This could be done by evaporating the solution to dryness and applying the Wadsworth method to the residue. Moir and Hinks⁹ extracted theobromine from aqueous solution by shaking with successive quantities of chloroform, and Parkes and Parkes¹⁰ added 5 per cent. of phenol to the chloroform. The method of continuous extraction with a liquid-liquid extractor seemed to be more promising, and the apparatus shown in Fig. 1 was devised for this purpose. It is a Soxhlet extraction apparatus with the syphon tube replaced by a continuous overflow pipe. With the dimensions shown, the volume of the aqueous layer is about 130 ml. The special condenser adaptor has six nozzles with fine jets which ensure maximum contact of the condensed chloroform with the aqueous layer. If a sufficiently rapid reflux rate is maintained (about 50 ml. per minute), 0.3 g. of theobromine can be completely recovered from aqueous solution in less than $3\frac{1}{2}$ hours, although 5 hours were taken in practice. No advantage was gained by using a larger extractor; one of 400 ml. capacity required 8 hours to complete the extraction of 0.3 g. theobromine, and one of 800 ml. capacity needed 16 hours to extract a similar amount.

After extraction, the chloroform was distilled off leaving theobromine that was usually 90 to 92 per cent. pure. It was only slightly discoloured and contained caffeine and a trace of fat. Only the caffeine and fat could be removed by leaching with light petroleum; some of the other impurities could also be removed if tetrachloroethane and ether were used as at the end of the Wadsworth process, but no more than 98 per cent. purity could be attained by this means. All attempts to produce pure theobromine failed. The purity of the crude theobromine as extracted above was therefore determined by the Boie¹² method; good sharp end-points have been consistently obtained with this quick and reliable method.

The following procedure is recommended. It has been in continual use in these laboratories for two years.

PREPARATION OF SAMPLE—

Cocoa beans or nib are ground to a mass and defatted with low-boiling (80° C.) light petroleum. The defatted material is dried and powdered before use. Mass or chocolate is defatted, dried and powdered. Press cake, extrusion cake or shell are ground before use, but cocoa powder requires no preparation. Cocoa residues containing added lime should first be neutralised with 3 *N* hydrochloric acid.

PROCEDURE

Well mix 10 g. of material with 5 g. of magnesia that has been heated to 900° C. and kept for use in a stoppered bottle. Transfer the mixture to a flask of 500 to 1000 ml. capacity, add 30 ml. of boiling water and boil under a reflux condenser for 10 minutes. Take care at the commencement of the boiling to control the frothing, which may become excessive. Clarify the hot liquid with 10 to 15 ml. of basic lead acetate (the strong solution of lead subacetate of the B.P.) and then filter the liquid by suction through a Buchner funnel with a 9 cm. Whatman No. 1 filter-paper. Wash the precipitate, which up to this point must not be allowed to go completely dry, with 50 ml. of hot water, and then suck dry. Transfer the residue and filter-paper to the flask, add 200 ml. of hot water and boil under reflux for 10 minutes. Filter the liquid and wash the precipitate as before. Repeat the extraction procedure once more. Concentrate the combined filtrates to about 100 g. in a tared flask, or in a flask marked at 100 ml.

During the concentration of the filtrate, prepare the clean and dry extractor by the addition of a one inch layer of dry glass wool on the bottom of the extractor tube. Weigh a 250-ml. ground joint flask containing three small fragments of porcelain. Add 100 to 120 ml. of chloroform, connect the extractor flask and clamp the apparatus vertically. Add chloroform to the extractor to a depth of three inches and then, through a funnel, add the 100 ml. of concentrated solution at a temperature of 50° to 60° C. The liquid displaces some of the chloroform into the flask. Wash the flask used for concentrating the solution with a small volume of hot water and add the washings to the extractor tube, taking care that the layer of chloroform above the glass wool is not less than an inch deep. Fit the dispersal

adaptor, the jets of which must be just below the surface of the aqueous phase. Add water, if necessary, until this condition is fulfilled.

Connect the apparatus to an efficient double surface condenser with ground joint and support the flask on an asbestos sheet having a circular hole large enough to take the bottom quarter- to half-inch of the flask. Do not use a gauze. Use an Amal burner practically full-on to give the necessary rapid rate of reflux. Make sure that, in addition to the jets of the adaptor being full, there is about a half-inch layer of chloroform in the body of the adaptor. For complete extraction, run the extraction for at least 5 hours. If it is intended to extract overnight, use an electrically heated sand-bath.

At the end of the extraction time, dismantle the apparatus and distil off the chloroform until a quarter-inch layer remains. Place the flask on a bath of boiling water and remove the remaining chloroform with a hand-blower, until there is no odour of chloroform. Dry the flask and weigh when cold.

Determine the theobromine in the crude extract by the Boie¹² method as follows—

Dissolve the crude extract in 100 ml. of water containing 1.5 ml. of *N* sulphuric acid by heating almost to boiling and maintaining at this temperature for 5 minutes. Cool the solution to 40° C. and add 1.5 ml. of phenol red indicator solution. Add *N* sodium hydroxide (approximately 1.5 ml.) until the solution turns red. Bring the colour back just to yellow by the careful addition of 0.10 *N* sulphuric acid. Add 0.10 *N* silver nitrate (which must be neutral to phenol red), taking care that the amount used in ml. is about 80 times the weight of crude theobromine in grams, *e.g.*, for 0.2 g. use 16 ml. of 0.10 *N* silver nitrate. Titrate the solution with 0.10 *N* sodium hydroxide until the pink colour returns. The end-point is indicated by a marked change in colour with one drop of the alkali solution.

1 ml. of 0.10 *N* sodium hydroxide \equiv 18.01 mg. of theobromine.

Express the theobromine as a percentage of the original material; for beans, nib, mass or chocolate, the fat percentage is also required for the purpose of calculation.

The results have been compared with those obtained by the Wadsworth method on various cocoa products. Some typical figures, expressed on moisture and fat-free material, are given in Table I.

TABLE I

Material used	Wadsworth method		Proposed method	
	Theobromine, %		Theobromine, %	
	Crude	Pure	Crude	Pure
Cocoa residue after solvent extraction of the fat				
(1)	3.14	2.98	3.33	3.05
(2)	3.05	2.93	3.31	3.00
(3)	3.12	3.03	3.37	3.05
(4)	3.30	3.14	3.45	3.15
(5)	3.24	3.06	3.37	3.11
(6)	3.25	3.14	3.53	3.17
(7)	3.23	3.11	3.41	3.12
(8)	3.28	3.19	3.48	3.21
(9)	2.65	2.58	2.81	2.59
(10)	2.81	2.75	3.03	2.76
Cocoa shell—				
Unroasted	1.58	1.53	1.71	1.54
Roasted	1.65	1.58	1.75	1.59
Roasted	1.12	1.04	1.19	1.06
Cocoa residues from theobromine extraction ..				
	0.55	0.53	0.59	0.54
	0.40	0.38	0.45	0.41
	0.74	0.71	0.78	0.71
Cocoa expeller cake				
	3.36	3.24	3.60	3.25
	3.31	3.19	3.52	3.19
	2.71	2.62	2.84	2.64
Milk chocolate				
	0.26	0.23	0.26	0.24
Plain chocolate				
	1.28	1.18	1.29	1.18
Cocoa powder				
	3.46	3.30	3.65	3.32

These figures show that the proposed method gives results that are as good as, and sometimes higher than, those obtained by the Wadsworth method. The validity of the method has been checked as follows—

(1) Theobromine of known purity was carried through the process with and without cocoa material. Some of the results obtained are given in Table II.

TABLE II

Pure theobromine added, g.	Theobromine in cocoa material used, g.	Theobromine found, g.	
		Crude	Pure
0.2471	nil	0.250	0.247
0.3014	nil	0.305	0.302
0.0592	0.282	0.368	0.3416
0.1026	0.224	0.356	0.327
0.1040	0.041	0.158	0.145
0.1327	0.041	0.192	0.174

These figures show that no theobromine is lost in the course of the process.

(2) Reproducible results have been obtained, as shown in Table III.

TABLE III

Material used	Theobromine found in 10 g.	
	Crude, g.	Pure, g.
Cocoa residue from solvent plant—Sample A ..	0.312	0.285
	0.311	0.284
	0.311	0.286
	0.313	0.285
	0.326	0.294
Ditto—Sample B	0.325	0.292
	0.324	0.293
	0.045	0.041
Cocoa residue from theobromine extraction ..	0.047	0.042

(3) *Blank determinations*—When blank determinations have been carried out, no weighable extract has been obtained, and less than 0.02 ml. of 0.10 N sodium hydroxide has been needed in the Boie assay.

SUMMARY

A method is proposed for the determination of theobromine in cocoa products. It is based upon the extraction of cocoa material with boiling water and magnesia, clarification, filtration and continuous extraction of the concentrated filtrate with chloroform for 5 hours. A design is given for a rapid liquid-liquid extractor for this purpose. The chloroform extract is assayed by the Boie method. The proposed method has been compared with the Wadsworth process.

The author wishes to thank the Directors of Messrs. Cadbury Bros., Ltd. for permission to publish this paper, and he is indebted to Mr. S. B. Phillips and to Dr. H. C. Lockwood for much helpful advice and guidance.

REFERENCES

1. Wadsworth, R. V., *Analyst*, 1921, **46**, 32.
2. Macdonald, J. A., "6th Ann. Rep. Cocoa Res.," Imp. Coll. Trop. Agriculture, 1936, p. 34.
3. Humphries, E. C., "8th Ann. Rep. Cocoa Res.," Imp. Coll. Trop. Agriculture, 1938, pp. 36-38.
4. Kay, J., and Haywood, P. J. C., *Analyst*, 1946, **71**, 162.
5. Lowe, E. H., *Ibid.*, 1948, **73**, 679.
6. Jalade, *Ann. Falsif.*, 1929, **22**, 396.
7. Pritzker, J., and Jungkunz, R., *Mitt. Lebensm. Hyg.*, 1943, **34**, 185.
8. Martin, F., and Clergue, H., *Ann. Chim. Analyt.*, 1942, **24**, 202.
9. Moir, D. D., and Hinks, E., *Analyst*, 1935, **60**, 439.
10. Parkes, A. E., and Parkes, H. A., *Ibid.*, 1937, **62**, 791.
11. Moores, R. G., and Campbell, H. A., *Anal. Chem.*, 1948, **20**, 40.
12. Boie, H., *Pharm. Ztg.*, 1930, **75**, 968.

The Determination of Trichloroacetic Acid in Urine

BY R. FRANT AND J. WESTENDORP

SYNOPSIS—Two methods are described for the estimation of trichloroacetic acid in urine, a semi-quantitative method with a possible error of about 25 per cent., and a more quantitative method with an average deviation of 5 per cent. Both methods are based on the well known Fujiwara reaction. Attention is drawn to the effect of carbon dioxide on the coloured solution.

The final method proposed is suitable for samples having a minimum concentration of 10 μg . of trichloroacetic acid per ml.

In view of the widespread use of trichloroethylene, a simple method for following its ingestion and excretion by industrial workers is of value.

Studies of the metabolism of trichloroethylene^{1,2} have shown that it is converted into trichloroacetic acid. Any scheme of analysis must therefore determine trichloroethylene in air, blood and urine, and also trichloroacetic acid in blood and urine.

Several excellent methods^{3,4,5,6,7} exist for the determination of trichloroethylene in the various media; we have, therefore, restricted our work to the determination of trichloroacetic acid in urine.

EXPERIMENTAL

Direct application of the well-known Fujiwara reaction^{3,4} gave orange colorations which were visually compared with a range of coloured papers. By this means standards were established equivalent to the range 1.5 mg. to 6 mg. of trichloroacetic acid per litre. This range proved insufficient to accommodate all the specimens received and it was found necessary to dilute the samples with urine free from trichloroethylene and trichloroacetic acid.

It was noticed that, on standing, the pyridine layer changed colour from orange to yellow and this has been shown to be due to reaction with the carbon dioxide in the air; if this is excluded, the layer is orange. The method finally adopted was as follows.

DIRECT METHOD—

Procedure—To 20 ml. of urine add 10 ml. of 12.5 *N* sodium hydroxide and mix. Pour the mixture on to 4.0 ml. of pyridine contained in a test tube. Close the mouth of the tube with a rubber bung with a tube leading to an absorption apparatus containing potassium hydroxide. Heat to 70° C. for exactly 5 minutes, and cool rapidly. Compare the red-orange coloration of the pyridine layer with a previously standardised series of coloured papers.

Traces of trichloroacetic acid too small for determination by this means may be detected by passing a stream of carbon dioxide through the pyridine layer. A colour change from orange to yellow may then be perceived at a concentration as low as 1 mg. of trichloroacetic acid per litre.

Table I shows the results obtained when this method was applied to a series of artificial standards. Apart from poor reproducibility this method suffers from the need for dilution with normal urine of samples containing large amounts of trichloroacetic acid. It was, therefore, decided to adapt the method to photometric determination.

PHOTOMETRIC METHOD—

The existence of two phases was considered a hindrance to successful photometric determination and attention was turned to the possibility of obtaining a single phase as in the process developed by Rogers and Kay⁷ for the estimation of carbon tetrachloride in air. The difficulty in applying this method to the determination of trichloroacetic acid in urine lay in the necessity of obtaining the chloro-compounds in acetone solution.

Fortunately, acetone is immiscible with strongly alkaline aqueous solutions and we were thus able to obtain the required acetone solution by extracting alkaline urine with a measured volume of acetone.

The use of ether instead of acetone was suggested, but although this would enable us to dispense with the addition of alkali, it was felt that the high vapour pressure of ether and its partial miscibility with water made acetone the more satisfactory solvent.

During the investigation into the suitability of this extraction for photometric work the following procedure was employed.

TABLE I

RESULTS OF DIRECT METHOD APPLIED TO KNOWN SOLUTIONS OF TRICHLOROACETIC ACID

Amount added in 20 ml., μg.	Amount found, μg.	Error, %
40	45	+ 12.5
40	45	+ 12.5
40	45	+ 12.5
50	45	- 10
50	45	- 10
70	60	- 14
90	90	0
90	90	0
100	90	- 11
110	60	- 45
120	120	0
120	90	- 25
120	90	- 25
140	120	- 14

Procedure—To 25 ml. of urine add 10 ml. of 12.5 N sodium hydroxide and 10 ml. of acetone. Shake vigorously for 5 minutes, and transfer 2 ml. of the acetone layer by means of a pipette into a test tube. Add 4 ml. of alkaline pyridine solution (100 ml. of pyridine, 40 ml. of water, 0.48 ml. of 15 per cent. sodium hydroxide) and heat the tube at 70° C. for exactly 5 minutes, and then cool with running water. Immediately after cooling, transfer the coloured solution to a 5-mm. cell and measure its extinction at 5400 A. with a Bleeker photo-electric colorimeter.

Visual comparison of repeated acetone extracts from a single sample of urine led us to believe that almost complete separation of trichloroacetic acid and trichloroethylene was achieved with only a single extraction. The results obtained by single extraction are shown in Table II; they suggest that Beer's law is followed by the coloured solution.

TABLE II

RESULTS OF SINGLE EXTRACTIONS OF SAMPLES OF URINE CONTAINING VARIOUS AMOUNTS OF TRICHLOROACETIC ACID

Trichloroacetic acid, μg./ml. (= C)	E	E - E ₀	$\frac{E - E_0}{C} \times 10^4$
0	0.054	} E ₀	
0	0.037		
10	0.122	0.076	76
10	0.123	0.077	77
20	0.204	0.158	79
20	0.198	0.152	76

A study was next made of the effect of variation in the time of heating the pyridine-acetone mixture; the results are shown in Table III. It is clear from this table that the

TABLE III

EFFECT OF VARIATION IN TIME OF HEATING

Trichloroacetic acid, μg./ml. (= C)	Heated for 5 minutes			Heated for 10 minutes		
	E	E - E ₀	$\frac{E - E_0}{C} \times 10^4$	E	E - E ₀	$\frac{E - E_0}{C} \times 10^4$
0	0.040			0.040		
0	0.043			0.043		
30	0.226	0.184	61	0.259	0.217	72
30	0.223	0.181	60	0.258	0.216	72
40	0.295	0.253	63	0.326	0.284	71
40	0.293	0.251	63	0.334	0.292	73

time of heating is an important factor. The fact that the values $(E - E_0)/C \times 10^4$ are lower in Table III than in Table II is attributed to variation in the alkali content of the pyridine-sodium hydroxide mixture and we suggest that more consistent results might be obtained by mixing 100 ml. of pyridine with 40 ml. of 0.18 per cent. sodium hydroxide.

The application of the method to urines containing large amounts of trichloroacetic acid with heating for 7 minutes gave the results shown in Table IV.

TABLE IV

RESULTS OBTAINED ON URINES CONTAINING LARGE AMOUNTS OF TRICHLOROACETIC ACID

Heating time = 7 minutes

Trichloroacetic acid, $\mu\text{g./ml.}$	E	$E - E_0$	$\frac{E - E_0}{C} \times 10^4$
0	0.034		
0	0.043		
30	0.213	0.174	58
30	0.217	0.178	59
60	0.387	0.348	58
60	0.409	0.370	62
90	0.611	0.572	64
90	0.639	0.600	67
120	0.841	0.802	67
150	1.020	0.980	65
150	1.020	0.980	65

APPLICATION TO HIGH CONCENTRATIONS—

An attempt to apply the method to higher concentrations by diluting the acetone before taking an aliquot proved unsatisfactory as the extract became turbid on the addition of pure acetone.

This difficulty was overcome by diluting the acetone extract with the acetone extract from a trichloroacetic acid- and trichloroethylene-free urine. The results given in Table V were obtained with a urine containing 120 $\mu\text{g.}$ of trichloroacetic acid per ml.

TABLE V

RESULTS OBTAINED AFTER DILUTION WITH ACETONE EXTRACT FROM TRICHLOROACETIC ACID- AND TRICHLOROETHYLENE-FREE URINE

Acetone extract, ml. (= a)	Blank extract, ml.	E	$E - E_0$	$\frac{E - E_0}{120} \times \frac{2}{a} \times 10^4$
2	0	1.010	0.977	82
2	0	1.020	0.987	82
1.6	0.4	0.716	0.683	71
1.6	0.4	0.773	0.740	77
1.2	0.8	0.601	0.568	79
1.2	0.8	0.608	0.575	80
0.8	1.2	0.423	0.390	81
0.8	1.2	0.420	0.387	81
0.4	1.6	0.238	0.205	85
0	2.0	0.030		
0	2.0	0.036		

These results suggested that analysis of a urine sample containing an unknown amount of trichloroacetic acid might be successfully carried out by this method, provided that a urine containing a known amount of trichloroacetic acid were examined concurrently to serve as a standard. The method was found to be improved by closing the mouth of the test tube with a plug of cotton wool containing solid potassium hydroxide to remove carbon dioxide from the atmosphere during the colour development, and by adding 1 ml. of boiled water to prevent turbidity.

We thus had two methods applicable to urine samples containing large amounts of trichloroacetic acid, *viz.*, (a) to dilute the sample with trichloroacetic acid-free urine, and (b) to take an aliquot from the acetone extract.

A sample was taken, which a semi-quantitative examination by the method already outlined had shown to contain about 600 $\mu\text{g.}$ of trichloroacetic acid per ml., and was examined by both methods. The results are shown in Tables VI and VII.

TABLE VI
RESULTS ON DILUTED SAMPLE

Sample, ml. (= p)	Trichloroacetic acid-free urine, ml.	E	E - E ₀	$\frac{E - E_0}{p} \times 10^3$	μg./ml.
0	25	0.009			
0	25	0.009			
1	24	0.152	0.143	143	671
1	24	0.155	0.146	146	684
2	23	0.261	0.252	126	591
2	23	0.261	0.252	126	591
3	22	0.383	0.374	125	586
3	22	0.386	0.377	126	591
4	21	0.533	0.524	131	615
4	21	0.500	0.491	123	577
5	20	0.627	0.618	124	582
5	20	0.651	0.642	128	600
Sample containing 60 μg./ml.			0.320		609

TABLE VII
RESULTS ON ACETONE EXTRACT OF SAME SAMPLE

Acetone extract sample, ml. (= q)	Blank extract, ml.	E	E - E ₀	$\frac{E - E_0}{q} \times 10^2$	μg./ml.
0	2.0	0.009			
0	2.0	0.009			
0.2	1.8	0.292	0.283	142	533
0.2	1.8	0.293	0.284	142	533
0.4	1.6	0.578	0.569	142	533
0.4	1.6	0.580	0.571	143	536
Sample containing 60 μg./ml.			0.320		534

A series of urines was then examined to determine the accuracy of the method; the results of this examination are shown in Table VIII. These results were considered satisfactory and the final method is given in detail below.

TABLE VIII
EXAMINATION OF ACCURACY OF METHOD

Trichloroacetic acid added, μg./ml.	Test	Blank	E	E - E ₀	Trichloroacetic acid found, μg./ml.	Error, %
40	2	0	0.206	0.200	36.4	- 9.0
40	2	0	0.218	0.212	38.5	- 3.6
80	2	0	0.429	0.423	76.6	- 4.0
80	2	0	0.405	0.399	72.4	- 9.5
133	2	0	0.736	0.730	132.5	- 0.4
133	2	0	0.717	0.711	129.0	- 3.2
120	1	1	0.330	0.324	117.5	- 2.0
120	1	1	0.318	0.312	113.1	- 5.6
173	1	1	0.486	0.480	174	+ 0.6
173	1	1	0.484	0.478	173.5	+ 0.3
214	1	1	0.605	0.599	217.5	+ 1.7
214	1	1	0.555	0.549	199	- 7.0
213	0.5	1.5	0.318	0.312	216	+ 1.4
213	0.5	1.5	0.286	0.280	203	- 4.7
254	0.5	1.5	0.365	0.359	260.2	+ 2.9
254	0.5	1.5	0.321	0.315	228.5	- 9.6
267	0.5	1.5	0.357	0.351	254	- 4.5
267	0.5	1.5	0.352	0.346	251	- 6.0
Blank	0	2.0	0.007			
Blank	0	2.0	0.005			
Standard	2	0	0.342	0.336	60.0	
Standard	2	0	0.332	0.326		

Average deviation 4.3

METHOD

REAGENT—

Alkaline pyridine reagent—A solution containing 100 ml. of pyridine, 40 ml. of water and 0.48 ml. of 15 per cent. sodium hydroxide.

PROCEDURE—

To 25 ml. of the specimen, add 10 ml. of 12.5 *N* sodium hydroxide and 10.0 ml. of acetone. Agitate the whole vigorously for exactly 5 minutes. Also carry out this procedure on a trichloroacetic acid-free urine and on 24 ml. of trichloroacetic acid-free urine to which has been added 1 ml. of 0.15 per cent. trichloroacetic acid solution.

Transfer 2-ml. portions of the acetone extract into test tubes by means of a pipette. If the amount of trichloroacetic acid is high, take a smaller quantity from the sample extract and dilute to 2 ml. with acetone from the blank determination.

Add 4 ml. of alkaline pyridine reagent and close the tubes with a plug of cotton wool containing a little solid potassium hydroxide. Heat the tubes at 70° C. in a water-bath for 7 minutes, remove them from the bath and rapidly cool to room temperature under running water. Lift the cotton wool plugs, add 1.0 ml. of boiled water from a burette and replace the plugs. Finally transfer the coloured solutions to 5-mm. cells and record their extinction by means of a Bleeker photo-electric colorimeter and using a wavelength of 5400 Å. The trichloroacetic acid in the sample (or samples) may be determined by comparison of the extinction of the sample with that of the standard.

This method is suitable for samples having a minimum concentration of 10 µg. of trichloroacetic acid per ml.

REFERENCES

1. Barrett, H. M., and Johnston, J. H., *J. Biol. Chem.*, 1939, **127**, 765.
2. Powell, J. F., *Brit. J. Ind. Med.*, 1945, **2**, 142.
3. Forssman, S., *Svenska Lakartidn.*, 1945, **29**, 1.
4. Fujiwara, K., *S.B. Naturf. Ges. Rostock.*, 1914, **6**, 33.
5. Jacobs, M. B., "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Interscience Publishers, Inc, New York, 1941.
6. Burgen, A. S. V., *Brit. Med. J.*, 1948, **1**, 1238.
7. Rogers, G. W., and Kay, K. K., *J. Ind. Hyg. Toxicol.*, 1947, **29**, 229.

THE MEDICAL DEPARTMENT AND ANALYTICAL LABORATORY
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December, 1949

The Micro-Gravimetric Determination of Lead in White Metals, Fusible Alloys and Tin-Free Copper-Base Alloys

BY CHRISTINA C. MILLER AND LESLIE R. CURRIE

SYNOPSIS—Lead (0.2 to 5 mg.) is separated from other alloy components, except copper in excess of 1 mg., by precipitating it twice as the lead nitrate - thiourea complex. The latter is dissolved in water, lead sulphide precipitated, separated, and dissolved in hydrochloric acid, and, finally, lead nitrate formed, which is dissolved in an aqueous solution of ammonium acetate, and filtered. The solution is acidified with acetic acid and lead separated and weighed as lead chromate, which is dried at 140° C.

The method is applied to 5 mg. amounts of white metals and a fusible alloy, which are dissolved in hydrochloric acid and nitric acid.

When more than 1 mg. of copper is present with lead, it must first be removed by electro-deposition. The method is then applicable to tin-free copper-base alloys, 5 to 10 mg. quantities of which are dissolved in nitric acid.

ON the micro-scale lead has been determined as lead sulphate, picrolonate, phosphate and dioxide,¹ but there have been few applications in alloy analysis. Strebinger² determined lead in lead - tin solders as lead sulphate. Lindsey³ and his collaborators are working out a comprehensive scheme of analysis for alloys, based on micro-electrolytic depositions, but so far no results for the determination of lead in alloys have been published.

Our objective was to devise a procedure for lead that could be applied to the determination of 2 to 90 per cent. in 5 to 10 mg. quantities of some non-ferrous alloys. For white metals and a fusible alloy we have adapted to the micro-scale and suitably modified the procedure used by Mahr and Ohle,⁴ whereby lead is precipitated as the lead nitrate - thiourea complex and, after appropriate treatment, converted into lead chromate as the weighing form. In the analysis of copper-base alloys containing little or no tin, we have removed copper by electro-deposition before applying the method.

EXPERIMENTAL

Mahr and Ohle showed that 20 to 50 mg. of lead contained in about 100 ml. of 1 to 2 *N* nitric acid could be quantitatively separated from comparable amounts of nearly all the common metals if the solution were saturated with thiourea and maintained at a temperature of 0° C. In the presence of bismuth a second precipitation was necessary, and in the presence of copper and silver, an adequate excess of thiourea. Aqua regia could be used without objection for the solution of alloys containing antimony and tin. The precipitates were separated, washed and dissolved in hot water, and in the resultant, almost neutral solution, after the addition of ammonium acetate, lead was precipitated as lead chromate. They applied the method to a lead - tin solder, a fusible alloy, a brass and a bronze. The simplicity of the method was attractive for micro-analysis because it seemed that, by using centrifugal methods of separation and the filter-stick technique, one might be able to carry out all the operations in one vessel.

In preliminary experiments many difficulties arose when we tried to apply the method microchemically. As solubility losses were easily incurred with lead nitrate - thiourea, the volume of the solution in which its precipitation was effected had to be made a minimum, partly in order to counterbalance the effect of having to use proportionately more wash solution on the micro-scale. In consequence of this the tendency for the precipitate to be contaminated with other metals was greater. Karaoglanov and Michov⁵ effected the separation of lead from moderate amounts of other metals by precipitating lead chromate from solutions 0.06 *N* in nitric acid. When we applied the method to lead in the solutions obtained from contaminated lead nitrate - thiourea precipitates difficulties arose because, in adjusting the acidity by neutralising the solution with ammonium hydroxide and adding a calculated amount of nitric acid, a precipitate of metallic sulphides separated. When this precipitate was dissolved, the resulting solution was contaminated by sulphur, which made lead chromate

difficult to filter. Reduction of excess chromate also occurred during the digestion that preceded filtration. Lastly, no satisfactory results could be obtained with small amounts of lead and the method was ultimately abandoned in favour of precipitation of lead chromate in solutions containing acetic acid and ammonium acetate, as was used by Mahr and Ohle. This meant that lead had first of all to be separated *completely* from other alloy components, as a rule by double precipitation with thiourea.

Since partial decomposition of thiourea caused contamination of lead chromate, it was necessary to eliminate it before precipitating the latter. This was achieved by precipitating lead as sulphide, dissolving it in hydrochloric acid, expelling hydrogen sulphide and then converting lead chloride into lead nitrate by evaporation with nitric acid. As some lead sulphate was invariably produced it was essential to dissolve the residue obtained after evaporation in a concentrated solution of ammonium acetate. Filtration of its solution was still required in order to remove a slight turbidity, and, in alloy analysis, to remove a little hydrated stannic oxide. The filtrate was collected in the vessel in which the lead was to be determined as lead chromate. Guzelj⁶ has shown that lead sulphate dissolved in ammonium acetate solution can be satisfactorily determined as lead chromate. The reagents were as far as possible AnalaR. Thiourea was recrystallised from water.

PROCEDURE FOR THE SEPARATION OF LEAD AS LEAD NITRATE - THIOUREA AND ITS DETERMINATION AS LEAD CHROMATE

Place the solution containing 0.2 to 5 mg. of lead as lead nitrate in a test tube (75 mm. × 12 mm.) and make up to a volume of 1.5 ml. that is 2 *N* in nitric acid. Add 0.2 g. of thiourea, shake the tube until precipitation starts, then cool it for half an hour at -5°C ., shaking vigorously at intervals. Centrifuge, while maintaining the temperature below 0°C . by placing the tube within a wider container of cooling liquid, that fits into the metal bucket of the centrifuge. Withdraw the centrifugate by suction through a sintered porcelain filter-stick and wash the precipitate once with 0.5 ml. of 2 *N* nitric acid that has been saturated with thiourea at room temperature and cooled to -5°C . Next dissolve the precipitate by placing the test tube containing it within a suitable suction apparatus and drawing 1.5 ml. of hot water through the filter into the tube.⁷ Add sufficient 7 *N* nitric acid to the solution to make it 1 to 2 *N*, add a small amount of thiourea, and repeat the above treatment, washing the precipitate thrice with 0.5-ml. portions of the prescribed solution before dissolving it.

In order to precipitate lead sulphide, add to the solution 0.5 ml. of 15 *N* ammonium hydroxide, saturate with hydrogen sulphide, cool to room temperature and centrifuge and withdraw the supernatant liquid as before. Wash the precipitate twice with 0.25 ml. of a saturated solution of hydrogen sulphide, then dissolve it by drawing 1.5 ml. of boiling 5 *N* hydrochloric acid through the filter-stick into the test tube. Heat to effect complete solution and evaporate the solution to dryness on the steam-bath, accelerating evaporation by means of a current of purified air. Dissolve the residue in 1 ml. of 7 *N* nitric acid, re-evaporate to dryness and dissolve again in 0.25 ml. of a hot, 20 per cent. ammonium acetate solution. Transfer the solution through a clean, porcelain filter-stick into a 5-ml. beaker that has been weighed together with a sintered glass (porosity No. 4) or asbestos-packed Emich type filter-stick. Wash the test tube, etc., twice with 0.25 ml. of hot water followed by 0.1 ml. of ammonium acetate solution, and finally twice with 0.25 ml. of hot water.

If the amount of lead is small (0.2 mg.) reduce the volume to less than half by evaporation. Whatever the final volume, make the solution 0.25 to 0.7 *N* in acetic acid, heat to boiling and precipitate lead chromate by the dropwise addition of a 0.5 per cent. solution of potassium dichromate, in amount ranging from 1.5 ml. for 5 mg. of lead, to 0.1 ml. for 0.2 mg. Digest the precipitate at 90°C . for 10 minutes then let it cool for 1 hour and filter. Wash a large precipitate once with 0.5 ml. of hot water and five times with 0.25 ml., and a small precipitate once with 0.3 ml. and then three times with 0.25 ml. Dry the beaker and its contents at 140°C . in a Benedetti - Pichler drying block, cool and weigh, with strict adherence to the programme outlined in the next section.

THE TREATMENT OF BEAKERS AND FILTER-STICKS BEFORE WEIGHING

Trouble caused by the production of electrostatic charges on glassware that had been wiped, prior to weighing, in accordance with Pregl's well-known procedure, led us to abandon this in favour of another routine, which also compensated for changes in barometric pressure. The tare for each beaker and filter-stick was another beaker of the same glass, adjusted to

weight by the addition of short lengths of glass rod. The outside of the prepared beaker and its counterpoise were wiped once with a pair of very damp flannelette cloths, one held in each hand, a rotary motion being imparted to the wiping, and then similarly with a pair of slightly damp pieces of chamois leather. Each beaker, held by forceps, was next passed four times through a non-luminous flame in order to dispose of any electrostatic charge, and then placed in the drying apparatus at 140° C. for 10 minutes. After removal, the beakers were cooled for 5 minutes on metal blocks, and the tip of the filter, which had been connected by rubber tubing to the suction line, was wiped clean. Both beakers were then placed for 15 minutes in a desiccator containing a saturated solution of calcium nitrate, which allowed the glass surfaces to assume rapidly a reproducible film of moisture.⁸ Finally, they were transferred simultaneously to the balance case and weighed after 5 minutes. A reliable duplicate of the first weighing was obtained by merely reheating (no suction) and cooling both beakers as before. After use the beaker and filter-stick were submitted to the full treatment, but the counterpoise, which had been kept in the desiccator, was only given the heating at 140° C. All weighings must be duplicated.

THE DETERMINATION OF LEAD IN ALLOYS

Method 1. For white metals and fusible alloys—Dissolve 5 mg. of the alloy in 0.2 ml. of 5 *N* hydrochloric acid and the minimum amount of 7 *N* nitric acid, add 1 ml. of water and sufficient 7 *N* nitric acid to bring its concentration to about 2 *N*. Proceed with the determination of lead as already indicated, noting, however, that with fusible alloys *both* precipitates of lead nitrate - thiourea must be washed thrice.

Method 2. For copper-base alloys containing little or no tin—Copper, which in excess of 1 mg. accompanied lead nitrate - thiourea, was removed initially by electro-deposition as follows. Dissolve 5 to 10 mg. of the alloy, contained in the usual test tube, in 0.2 ml. of 7 *N* nitric acid, add 2.5 ml. of water and boil to expel nitrous acid. Next add 0.1 ml. of a 10 per cent. urea solution and electrolyse for 10 minutes at 2.5 volts, using as a cathode a cylinder (diameter 10 mm., height 15 mm.) of platinum gauze (20 strands per cm.), and, as an anode, a platinum wire. Finally remove and rinse the electrodes, carefully protecting the anode on which some lead dioxide deposits. Evaporate the solution to dryness on a steam-bath and take up the residue in 0.2 ml. of 5 *N* hydrochloric acid. Dissolve the lead dioxide on the anode in dilute nitric acid containing hydrogen peroxide and collect the solution in the test tube, to make a final volume of 1.6 ml. at a concentration of about 2 *N* in nitric acid. Precipitate lead nitrate - thiourea once only and continue as described above.

RESULTS

(i) *The direct determination of lead as lead chromate*—Weighed portions of a standard solution of lead nitrate, prepared from "British Chemical Standards" lead, gave the following results, when the theoretical factor of 0.6411 was used for converting lead chromate into lead.

TABLE I

Weight of lead taken, mg.	Number of experiments	Maximum range in error, $\mu\text{g.}$	Average error, $\mu\text{g.}$
5	4	+6 to -5	-1
1	9	+9 to -5	-3
0.2	10	+5 to -7	nil

No significant difference was noted when the amount of ammonium acetate present was varied between 20 and 100 mg., or when the amount of acetic acid ranged between 0.25 and 0.7 *N*, provided that the washing of the lead chromate was very carefully done. A negative error averaging 4 to 5 $\mu\text{g.}$ was incurred when the smallest quantity of lead was precipitated with chromate in the same volume of solution as the larger quantities.

(ii) *The determination of lead as lead chromate after first separating it as lead nitrate - thiourea*—Weighed portions of the above standard solution of lead nitrate were submitted to the full scheme of separations previously outlined and the following results obtained. In a "blank" run on the reagents no lead was found.

Error on 5 mg. of lead, -22, -20, +13 and +7 $\mu\text{g.}$

Error on 0.2 mg. of lead, -2, -19, +4 and -11 $\mu\text{g.}$

Inadequate precautions for keeping the lead nitrate - thiourea precipitates cool during

centrifugation caused the rather large negative errors in the first pair of results for 5 mg. of lead, and incomplete mastery of the technique, at this stage, the irregularity in the results for 0.2 mg.

Influence of copper and bismuth—The presence of 50 μ g. of copper or bismuth did not affect the results for 5 mg. of lead. The maximum amount of copper that could be separated from 1 mg. of lead in 1.5 ml. of solution was 1 mg. Three mg. of bismuth could be separated from 1 mg. of lead if both precipitates of lead nitrate - thiourea were washed thrice with 0.5 ml. of the wash solution.

(iii) *Lead in alloys*—In order to avoid errors due to lack of homogeneity in the samples of prepared alloys, we prepared small amounts for analysis by aliquot partition of a solution made up from 1 g. of the powdered alloy and treated in accordance with the prescribed micro-procedure. The metals used in preparing the synthetic alloy solutions were the purest available; the lead, copper and zinc having a purity in excess of 99.95 per cent. The bismuth and cadmium were examined for lead and none was found.

All the results shown in Table II refer to 5 mg. of alloy, except for the high-speed brass where 10 mg. was taken. In the analyses of the copper-base alloys, copper was removed by electro-deposition before precipitating lead nitrate - thiourea.

TABLE II

	Percentage composition					Percentage of lead found
	Sb	Sn	Bi	Cu	Pb	
White metal "A"* ..	12.04	4.64	0.03	0.33	82.6	82.9, 82.9, 82.7, 82.9
White metal "B"* ..	7.51	84.0	trace	4.08	3.86	3.65, 3.67, 3.65, 3.88§
Lead-base bearing metal†	10.09	10.91	0.06	0.05	78.9	78.7, 78.8
	Cd					
Fusible alloy‡ ..	12.5	12.5	50.0	—	25.00	25.00, 25.04, 24.79, 24.96
Bearing metal‡ ..	—	—	—	70.0	30.00	30.10, 30.02, 30.10, 30.00
	Zn					
High-speed brass‡ ..	37.0	—	—	60.0	3.00	3.03, 2.92, 2.94, 3.01

* British Chemical Standards sample.

† U.S.A. Bureau of Standards sample.

‡ Synthetic.

§ In all except the last experiment the lead nitrate - thiourea had been cooled for 15 minutes only instead of the recommended half hour.

The results in Table II show that the micro-gravimetric determination of lead in the alloys cited is practicable provided that the conditions prescribed on p. 468 are closely followed. A negative error is rather easily incurred in dealing with quantities of lead of the order of quarter of a milligram.

We gratefully acknowledge a maintenance grant to one of us (L. R. C.) from the Department of Scientific and Industrial Research and a grant from the Ritchie Fund for the purchase of apparatus.

REFERENCES

1. Hecht, F., and Donau, J., "Anorganische Mikrogewichtsanalyse," Edwards Brothers, Inc., Ann Arbor, Michigan, 1940, p. 150.
2. Strebinger, R., *Chem. Zentr.*, 1918, 11, 471.
3. Lindsey, A. J., *Analyst*, 1948, 73, 72.
4. Mahr, C., and Ohle, H., *Z. anorg. Chem.*, 1937, 234, 224.
5. Karaoglanov, Z., and Michov, M., *Z. anal. Chem.*, 1935, 103, 113.
6. Guzelj, L., *Ibid.*, 1936, 104, 107.
7. Hecht, F., and Donau, J., "Anorganische Mikrogewichtsanalyse," Edwards Brothers, Inc., Ann Arbor, Michigan, 1940, p. 101.
8. Thiers, R. E., and Beamish, F. E., *Anal. Chem.*, 1947, 19, 434.

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May, 1950

The Micro-Gravimetric Determination of Lead in Bronzes

By CHRISTINA C. MILLER AND LESLIE R. CURRIE

SYNOPSIS—Lead in amounts of 0.2 to 1 mg. is quantitatively separated under carefully controlled conditions from 5 to 10 mg. of copper and 1 mg. of tin, by depositing it electrolytically as lead dioxide from solutions containing hydrofluoric acid and nitric acid (*cf.* McCay¹). Lead dioxide is dissolved and lead precipitated and weighed as lead chromate.

The method is applied to 5 and 10 mg. amounts of two bronzes containing, respectively, 20 and 1.83 per cent. of lead.

WHEN the method described in the preceding paper, see p. 467, for the determination of lead in tin-free, copper-base alloys, was applied to those containing an appreciable amount of tin, no satisfactory results could be obtained. The average result for a bronze containing 20.00 per cent. of lead was 19.37, and for another containing 1.83 per cent., 1.69 per cent. In the final filtration that preceded the precipitation of lead chromate, hydrated stannic oxide was invariably withheld on the filter and it contained adsorbed lead. Although present in the original bronze solutions, stannic oxide dissolved in the hydrochloric acid subsequently added, but β -stannic salts apparently contaminated the lead nitrate - thiourea complex and lead sulphide, and gave rise again to hydrated stannic oxide in the final treatment with nitric acid.

Stannic oxide did not separate initially if tartaric or citric acid was included in the nitric acid solvent for the bronze, nevertheless it still appeared in the final solution. All efforts made to eliminate tin by volatilising its halides were unsuccessful. Attempts made to remove copper by depositing it electrolytically from hydrochloric acid solutions² of the alloys, in which β -stannic salts were not produced, unaccountably failed. The recovery of adsorbed lead from impure stannic oxide, by fusing the latter with sodium carbonate and sulphur and separating soluble sodium thiostannate from insoluble lead sulphide, was associated with complications of procedure that led to other negative errors of undetermined origin.

The object of our investigation was therefore to devise an alternative method for the determination of lead in bronzes. McCay¹ showed that 60 to 400 mg. of lead could be separated from up to 500 mg. of tin by depositing it anodically as lead dioxide from a solution containing nitric and hydrofluoric acids. We have evolved comparable micro-procedures for the separation of 1 and 0.2 mg. of lead from 1 mg. of tin and 5 mg. or more of copper, and applied them to the bronzes mentioned above, the lead being finally weighed as chromate.

EXPERIMENTAL

ELECTROLYTIC APPARATUS FOR THE ANODIC DEPOSITION OF LEAD DIOXIDE—

Electrolyses were conducted in a platinum crucible (height 26 mm., diameter at the top, 20 mm., and at the bottom, 13 mm.) as the anode, with a platinum gauze (10 strands per cm.) cylinder (height 13 mm., diameter 10 mm.) as the cathode. Several strands of platinum wire were placed across the bottom of the cylinder so that it formed a kind of basket. The effect of this was to induce the deposition of lead dioxide on the bottom of the crucible, which did not occur without this modification. To the upper edge of the cylinder was welded a platinum wire that was bent at right angles above the crucible and sealed into a glass support. The crucible rested in a triangle of platinum wire, which was attached to an insulated ring, and connected to the positive terminal of a 4-volt battery. The electrical circuit contained a 55-ohm, variable resistance and a milliammeter, and across the electrodes was a 5-volt voltmeter of 50,000-ohm resistance. The electrically driven stirrer was a platinum wire, slightly flattened at the lower end, and sealed into a glass rod at the upper. Attached to it just above the crucible, and rotating with it, was a protective celluloid cover. A moderate rate of stirring only was required. Vigorous stirring caused depositions to be incomplete. In order to obtain adherent deposits of lead dioxide the crucible was etched by brief treatment with aqua regia.

CONDITIONS FOR THE DEPOSITION OF LEAD DIOXIDE—

Quantitative deposition, especially of a small amount of lead, occurred under carefully controlled conditions that were deduced from the results of a long series of experiments, in which electrolyses were done in the presence of 5 to 10 mg. of copper and 1 mg. of tin. The method is as follows: Evaporate the solution containing nitrates and fluorides of the metals to dryness in the crucible to be used for the electrolysis and, if 1 mg. of lead is present, take up the residue in 2.5 ml. of a solution that is 1.5 *N* in nitric acid and 1.0 *N* in hydrofluoric acid. For 0.2 mg. of lead reduce the concentration of both acids to 0.5 *N*. Add 5 mg. of urea, set up the electrolysis outfit and start the stirrer. Begin the electrolysis at room temperature, with the full resistance in the circuit, and, after 1 to 2 minutes, increase the voltage to 2.50 ± 0.05 . Maintain this value for 30 minutes, then remove the stirrer, withdraw the electrolyte by suction and rapidly replace it with water. Remove and replace the water until no current is registered.

THE DETERMINATION OF LEAD AS LEAD DIOXIDE OR AS LEAD CHROMATE—

If the determination of lead as lead dioxide is required, proceed as follows: Dry the crucible containing lead dioxide for 10 minutes in the platinum-lined cavity of a metal drying block maintained at 230° C., then cool for 5 minutes on a metal block and 5 minutes in the balance case, and weigh against a similar crucible as a counterpoise. Next dissolve the lead dioxide in 0.5 ml. of hot 7 *N* nitric acid and 0.1 ml. of 3 per cent. hydrogen peroxide solution, and, if the further determination of lead as lead chromate is required, transfer the solution to a 5 ml. glass beaker that has been previously weighed together with a sintered glass filter-stick (porosity No. 4). Wash the crucible first with half the above volumes of nitric acid and hydrogen peroxide and then five times with 0.25 ml. of hot water. Dry and weigh the crucible. For the determination of lead as lead chromate evaporate the solution in the beaker to dryness, dissolve the residue in 1.5 ml. of a 2 per cent. solution of ammonium acetate and 0.1 ml. of 7 *N* acetic acid, and proceed exactly as is described in the preceding paper.

THE DETERMINATION OF LEAD IN BRONZE—

In the crucible to be used for the electrolysis, dissolve 5 or 10 mg. of bronze in a mixture of 4 drops of water, 2 of hydrofluoric acid (40 per cent. w/w) and 3 of concentrated nitric acid. Evaporate the resulting solution to dryness and dissolve the residue in 2.5 ml. of a solution containing the amounts of nitric acid and hydrofluoric acid appropriate for the anticipated amount of lead. If a little antimony is present, oxidise it with a drop of a 0.5 per cent. solution of potassium dichromate (*cf.* McCay), then add 5 mg. of urea and proceed as already outlined.

RESULTS

The purity of the lead, tin and copper used in the following experiments exceeded 99.95 per cent. AnalaR reagents were employed throughout and examined when necessary for traces of lead. Stock solutions containing hydrofluoric acid were prepared and kept in platinum vessels.

Lead as lead dioxide—All depositions were effected in the presence of 5 or 10 mg. of copper and the amounts of nitric acid and hydrofluoric acid appropriate for the weight of lead. Weighed portions of a standard solution prepared by dissolving lead in nitric acid were used.

- Error on 1 mg. of lead, (a) Tin absent: +23, +20, +17, +21 and +17 μg .
 (b) 1 mg. of tin present: +36 and +28 μg .
 (c) 5 mg. of tin present: +13 and +28 μg .
 Error on 0.2 mg. of lead, (a) Tin absent: +8, +1, +9 and +6 μg .
 (b) 1 mg. of tin present: +4, +4, 0, +5 and +2 μg .

These errors, which are much in excess of what could be caused by our use of the theoretical factor for the conversion of lead dioxide to lead (*cf.* Sand³), are in accord with positive errors of about 2 per cent. found by McCay, who attributed them to fluoride contamination of the lead dioxide. He eliminated them by dissolving the lead dioxide and redepositing it in the absence of hydrofluoric acid. We inexplicably failed to improve our results by repeating the electrolysis in the presence of 5 mg. of copper and nitric acid only. The copper was added in the second electrolysis in order to prevent cathodic deposition of lead.

Influence of other elements—The addition of 50 μg . of phosphorus added as potassium dihydrogen phosphate had no significant adverse effect on the deposition of 0.2 or 1 mg. of lead as lead dioxide. If 200 μg . of manganese (II) or 100 μg . of antimony (V) were initially present with 1 mg. of lead, the amounts of manganese and antimony that were found in the lead dioxide were less than 1 and 3 μg . respectively. The influence of bismuth was considerable, 20 per cent. of that initially added accompanying the lead dioxide.

Lead as lead chromate—The following results refer to experiments in which 5 or 10 mg. of copper and 1 mg. of tin were initially present with the lead, which was deposited as lead dioxide and then dissolved and converted into lead chromate.

Error on 1 mg. of lead, -3, +2, +12 and -8 μg .

Error on 0.2 mg. of lead, +9, -1, -3, +10, -4 and +8 μg .

The excessive positive errors were attributed to the failure to filter the nitric acid solution of the lead dioxide. In the following analyses of bronzes, filtration was carried out through a sintered glass filter-stick (porosity No. 4).

Lead in bronzes as lead chromate—(1) High lead bronze. A synthetic solution was prepared by adding lead as lead nitrate to a nitro-hydrofluoric acid solution of British Chemical Standards Bronze "C," so that the percentage composition of the corresponding alloy was: copper 69.82, tin 7.88, antimony 0.03, bismuth a trace, other (non-interfering) elements 2.27 and lead 20.00. The weighed portions of the solution taken for analysis corresponded to about 5 mg. of alloy.

Lead found, 20.02, 20.02, 20.31 and 19.94 per cent.

(2) British Chemical Standards Bronze "A." A standard solution was prepared from 1 g. of bronze in accordance with the micro-procedure and weighed portions equivalent to 10 mg. of alloy were analysed. The percentage composition of the bronze was: copper 85.5, tin 9.7, antimony 0.24, other (non-interfering) elements 2.71 and lead 1.83.

Lead found, 1.81, 1.80, 1.84 and 1.81 per cent.

We gratefully acknowledge a maintenance grant to one of us (L. R. C.) from the Department of Scientific and Industrial Research and a grant from the Ritchie Fund for the purchase of apparatus.

REFERENCES

1. McCay, L. W., *J. Amer. Chem. Soc.*, 1914, **36**, 2375.
2. Lindsey, A. J., *Analyst*, 1938, **63**, 159.
3. Sand, H. J. S., "Electrochemistry and Electrochemical Analysis," Vol. II, Blackie & Son Ltd., London, 1940, p. 74.

CHEMISTRY DEPARTMENT
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May, 1950

Electrolytic Determination of Bismuth

By GEORGE NORWITZ

SYNOPSIS—An accurate electrolytic method for the determination of bismuth is described. The bismuth is electrolysed from a perchloric acid solution containing hydrazine sulphate. A preliminary separation of bismuth prior to the electrolysis is usually necessary.

THE methods previously proposed for the electrolytic determination of bismuth are not entirely adequate. Deposition at constant current has not proved satisfactory because of the difficulty of obtaining adherent deposits and complete deposition.^{4,9} Deposition of bismuth at controlled potential^{1,2,5,6,7,8} is an accurate method but requires apparatus that at present is available to few laboratories. An investigation by the author on the deposition of bismuth from various media resulted in the development of a constant-current method that has proved satisfactory. In this method the bismuth is electrolysed from a perchloric acid solution containing hydrazine sulphate. The latter reagent, which was found to ensure good electro-deposition of the bismuth and to prevent deposition of the bismuth on the

anode, has been recommended by Kny-Jones⁶ for the determination of bismuth at controlled potential using a sulphuric - nitric acid medium. With constant current, the use of hydrazine sulphate with a sulphuric - nitric acid medium, a sulphuric acid medium or a nitric acid medium was not successful.

EXPERIMENTAL

Various amounts of pure metallic bismuth were dissolved in 10 ml. of 70 per cent. nitric acid. Ten millilitres of 70 per cent. perchloric acid were added and the solutions evaporated until strong fumes of perchloric acid were evolved with the cover lids ajar. The solutions were diluted to 190 ml. with water, and 5 ml. of a saturated solution of hydrazine sulphate were added. The solutions were electrolysed at 1 ampere for 1 hour using tared platinum gauze cathodes, 60 mm. in height and 50 mm. in diameter, and platinum spiral anodes. During the electrolysis the solutions were stirred. The cathodes were immersed in water and then in alcohol, dried at 105° C. for 3 minutes, cooled and weighed. The results obtained for bismuth are shown in Table I.

TABLE I
RESULTS FOR BISMUTH IN BISMUTH METAL

Bismuth present, g.	Bismuth found, g.
0.0100*	0.0101
0.0100*	0.0103
0.0500*	0.0496
0.0500*	0.0502
0.1000	0.0997
0.1000	0.0996
0.2000	0.2004
0.2000	0.1999
1.0000	1.0002
1.0000	1.0006

* Aliquots of standard bismuth nitrate solution used.

Various amounts of bismuth were dissolved in 10 ml. of 70 per cent. nitric acid and an oxychloride precipitation made for the bismuth. The bismuth oxychloride precipitate was filtered, the paper and precipitate dissolved in 15 ml. of 70 per cent. nitric acid and 10 ml. of 70 per cent. perchloric acid and the solutions evaporated to strong fumes of perchloric acid. The solutions were diluted, hydrazine sulphate was added and the bismuth electrolysed as above. The results obtained are shown in Table II.

TABLE II
RESULTS FOR BISMUTH AFTER PRELIMINARY SEPARATION OF THE BISMUTH AS
THE OXYCHLORIDE

Bismuth present, g.	Bismuth found, g.
0.0100*	0.0103
0.0100*	0.0100
0.0500*	0.0497
0.0500*	0.0498
0.1000	0.1001
0.1000	0.0997
0.2000	0.2006
0.2000	0.2001
0.5000	0.5003
0.5000	0.4996

* Aliquots of standard bismuth nitrate solution used.

DISCUSSION OF RESULTS

In view of the scarcity of good methods for determining bismuth,³ the proposed electrolytic method should have considerable application. Because of the variable composition of the precipitate the weighing of bismuth as bismuth oxychloride "is permissible only when a few milligrams of bismuth is involved."³

A preliminary separation of the bismuth is normally necessary, as copper, silver, lead, mercury, cadmium, tin, antimony and arsenic will deposit with the bismuth. For this preliminary separation the oxybromide, sulphide, or carbonate methods may be used as well as the oxychloride method. Tin, antimony and arsenic may be volatilised with hydrobromic acid.

REFERENCES

1. Collin, E. M., *Analyst*, 1929, **54**, 654.
2. Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. Frederick Smith Chemical Co., Columbus, Ohio, 1948, p. 42.
3. Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," John Wiley & Sons, New York, 1929, p. 189.
4. — *Ibid.*, p. 192.
5. Kny-Jones, F. C., *Analyst*, 1939, **64**, 172.
6. — *Ibid.*, 1939, **64**, 575.
7. — *Ibid.*, 1941, **66**, 101.
8. Sand, H. J. S., *J. Chem. Soc.*, 1907, **91**, 373.
9. Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, 1943, p. 356.

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April, 1950

The Colorimetric Determination of Impurities in Titanium Metal

Iron and Manganese

By J. A. CORBETT

SYNOPSIS—The colorimetric methods for the determination of iron by thiocyanate and for manganese by oxidation to permanganate are applied to the direct determination of these metals in metallic titanium, and the conditions for their adaptation to the photo-electric absorptiometer are specified.

The procedures described are applicable to amounts below 2.0 per cent. for both metals, with a precision of ± 2 per cent. for iron and ± 1.0 per cent. for manganese.

METHODS have been developed for the estimation of small amounts of iron and manganese in titanium metal. Iron is estimated by the coloured thiocyanate-iron complex, and manganese by oxidation to permanganate with potassium periodate, the intensity of the colours being measured in a photo-electric absorptiometer. The methods cover the range 0 to 2.0 per cent. of iron and manganese, with an accuracy of ± 2 per cent. for the iron content and ± 1 per cent. for the manganese content.

IRON

The estimation of iron in the presence of titanium usually involves the precipitation of the iron with hydrogen sulphide in an alkaline tartrate solution. Iron can then be estimated by several available procedures. This paper is concerned with the estimation of iron directly in the presence of large amounts of titanium.

Haywood and Wood¹ have reported methods for the estimation of iron in copper alloys, aluminium and magnesium. The methods are based upon the coloured thiocyanate complex, but vary with respect to acid concentration, amount of oxidising agent and concentration of thiocyanate, which depend upon the particular metal present. Thornton² has outlined a colour comparison method for iron in titanium pigments, using thiocyanate, but Snell³ reports the formation of yellow titanium compounds with thiocyanates such as $K_2TiO(CNS)_4$ and $K_3Ti(CNS)_3 \cdot 6H_2O$.

EXPERIMENTAL INVESTIGATION

APPARATUS—

The photo-electric instrument used in this work consisted of a single photo-cell connected to a galvanometer with variable shunt resistors, and the light source was a tungsten-filament lamp operated from an accumulator.⁴

ACID CONCENTRATION—

Titanium is most satisfactorily dissolved in dilute sulphuric acid and hydrogen peroxide, the excess of hydrogen peroxide being finally destroyed in the hot sulphuric acid solution. Table I shows the effect of sulphuric acid concentration on the thiocyanate reaction in the presence of titanium and iron. In a 9 *N* sulphuric acid solution, the yellow colour of the titanium masked the iron complex. In an acid concentration of 0.7 *N*, however, the red colour of the iron complex was obtained, the titanium having no apparent effect.

TABLE I

EFFECT OF SULPHURIC ACID CONCENTRATION

100 ml. of solution containing 100 mg. of titanium, 0.12 mg. of iron and 2 per cent. of ammonium thiocyanate

Sulphuric acid concentration	Colour	Condition after standing for 15 minutes
0.7 <i>N</i>	red	faded
3 <i>N</i>	red-brown	faded
6 <i>N</i>	red-brown	faded
9 <i>N</i>	yellow	white precipitate
12 <i>N</i>	yellow	white precipitate

STABILITY OF COLOUR—

As shown in Table I, the colour faded rapidly; therefore ammonium persulphate was added to stabilise the colour. Table II shows the effect of adding various amounts of ammonium persulphate, a large excess of which was found necessary to prevent fading.

TABLE II

STABILITY OF IRON - THIOCYANATE COMPLEX

100 ml. of solution in *N* sulphuric acid, containing 2 per cent. of ammonium thiocyanate and 0.12 mg. of iron

Time	Ammonium persulphate added		
	nil	0.1 g. per 100 ml.	0.2 g. per 100 ml.
	Visual	Extinction coefficient*	Extinction coefficient*
10	visible	0.41	0.355
15	fading	0.40	0.355
20		0.36	0.360
25		0.355	0.355
35		0.35	0.355
45		0.34	0.360

* The reading on absorptiometer with green filter.

FILTERS—

Ilford "Wide Band" filters were used in this work and Table III gives results with two different filters, No. 623 (blue-green) with maximum transmission at 4950 Å., and No. 624 (green) with maximum transmission at 5200 Å. Filter No. 623 is the more sensitive, and covers a satisfactory range of concentrations.

RESULTS—

Typical results of analyses of titanium metal, prepared by the Kroll process, and titanium - iron alloys are shown in Table IV. The results are compared with those obtained by the normal volumetric method, in which iron was titrated with potassium dichromate after separation from titanium as sulphide. In the absorptiometric method 0.5-g. portions

TABLE III

COMPARISON OF FILTERS

Titanium present = 100 mg. per 100 ml.; 4-cm. cell

Iron content, mg. per 100 ml.	Extinction coefficient	
	With filter No. 623	With filter No. 624
0.05	0.21	0.15
0.105	0.435	0.31
0.13	0.54	0.39
0.15	0.62	0.445
0.18	0.78	0.535
0.21	0.865	0.615
0.23	0.97	0.70
0.25	1.30	0.74

were used, and the solution of titanium in sulphuric acid was diluted to 100 ml. and the colour was produced in 20-ml. aliquots of solution, as described in the method below. The estimation was performed in 1 hour, against 6 hours required for the volumetric procedure.

TABLE IV

COMPARISON OF RESULTS OBTAINED BY ABSORPTIOMETRIC AND VOLUMETRIC METHODS

Material	Iron found	
	By absorptiometric method, %	By volumetric method, %
ABP 40 mesh	0.150	0.150
	0.148	
ABP 100-250 mesh	0.130	0.130
	0.130	
ABP -250 mesh	0.230	0.230
	0.233	
AHS alloy	0.96	0.95
	0.955	
AHT alloy	2.02	2.03
	2.03	
AML alloy	1.05	1.07
	1.07	
AMN alloy	2.06	2.06
	2.06	

METHOD

REAGENTS—

Sulphuric acid—A solution of 300 ml. of 36 *N* sulphuric acid diluted with water to 1 litre

Ammonium thiocyanate—A 20 per cent. solution.

Ammonium persulphate—A 2 per cent. solution.

Hydrogen peroxide—A 10-volume solution.

PROCEDURE—

Transfer 0.5 g. of titanium (containing not more than 10 mg. of iron) to a 250-ml. squat beaker, add 30 ml. of 30 per cent. sulphuric acid, and warm until the reaction has ceased. Add hydrogen peroxide (10-volume solution) dropwise until the red-brown colour of the titanium complex is evident, and then evaporate until the solution is colourless and all the titanium is in solution (see Note 1, below). Cool and dilute to 60 ml. with water, and then boil the solution to dissolve any titanium salts. Re-cool and transfer to a 100-ml. standard flask and dilute to the mark.

Transfer a 20-ml. aliquot to a 100-ml. standard flask and add 40 ml. of water, 10 ml. of 2 per cent. ammonium persulphate solution and 10 ml. of 20 per cent. ammonium thiocyanate solution. Dilute to 100 ml. with water, mix, and allow the solution to stand for 15 minutes. Measure the absorption, using a cell of the correct size (see Note 2, below) and a blue-green filter of maximum transmission at 4950 Å.

Perform a blank determination on the reagents under the same conditions.

CALIBRATION GRAPH—

Standard iron solution—Dissolve 0.5 g. of pure iron in the minimum amount of sulphuric acid, add 3 ml. of hydrogen peroxide (10-volume solution), and evaporate to remove excess of hydrogen peroxide. Dilute the solution with water, and boil to dissolve the iron salts. Dilute to 1 litre; take 50 ml. of this solution and dilute to 500 ml.

1 ml. of this solution \equiv 0.05 mg. of iron.

Transfer 0.5 g. of titanium (iron-free or of known iron content) into a 250-ml. squat beaker. Treat as in the method until the 100 ml. of solution is obtained.

Measure 20-ml. aliquots into 100-ml. standard flasks and add to each a suitable amount of iron solution, to give the range of iron concentrations required. Add water and reagents in the same order as in the method, and measure the absorption of each solution. Perform a blank determination on the reagents and adjust the readings accordingly. Plot the extinction coefficient against iron concentration.

NOTES—

1. Prolonged fuming of the sulphuric acid will cause precipitation of titanium dioxide which will not dissolve.
2. The range of the cells is as follows—

Range, %	Cell length, cm.
0 to 0.25	4
0 to 0.50	2
0 to 1.00	1
0 to 2.00	0.5

Results obtained are within ± 2 per cent. of the iron content.

3. The presence of appreciable amounts of silica or any other insoluble material will require the introduction of a filtration treatment, and will necessitate the examination of this material for the possible presence of iron. Silica may be estimated in this fraction.

4. For calibration in the range of 0 to 2.0 per cent. of iron, prepare a standard solution of greater iron concentration by dissolving 1 g. of iron by the method given above. This solution contains 0.10 mg. of iron per ml., and this will help to preserve the correct concentration of acid.

MANGANESE

The separation of large amounts of titanium from manganese is an unsatisfactory procedure, owing to adsorption. Because of the convenience and speed with which manganese can be estimated in the presence of many other metals, a study was made of the prospects of a direct estimation in the presence of large amounts of titanium.

Methods for the absorptiometric estimation of manganese in ferrous alloys, etc., usually depend upon the oxidation of the manganese to permanganic acid either with persulphate and silver nitrate, or with potassium periodate. Hough³ has stated that in the presence of titanium, manganese is not completely oxidised with persulphate, but oxidations with potassium periodate and sodium bismuthate are satisfactory. No figures for the amounts of titanium involved are given, but as the work referred to the analysis of rocks it may be assumed that the amounts were not large.

EXPERIMENTAL INVESTIGATION

POTASSIUM PERSULPHATE—

Experiments with potassium persulphate and silver nitrate with 200 mg. of titanium and from 0.10 to 4.0 mg. of manganese in sulphuric acid solutions verified Hough's findings³ (see above).

SODIUM BISMUTHATE—

Guerin⁴ and the author have both found that in the presence of large amounts of titanium, manganese is not completely oxidised. Tests with 10 mg. of manganese in the presence of 500 mg. titanium gave 88.0 per cent. recovery of the manganese by the sodium bismuthate-ferrous sulphate titration method. This is to be the subject of a separate investigation.

POTASSIUM PERIODATE—

Table V gives absorptiometric readings on manganese solutions in the presence of titanium, compared with results from similar solutions containing no titanium. Manganese was oxidised with potassium periodate in a boiling sulphuric acid solution to which nitric acid had been added.

TABLE V

EFFECT OF TITANIUM ON THE OXIDATION OF MANGANESE WITH POTASSIUM PERIODATE

Manganese, mg.	Cell length, cm.	Extinction coefficient*	
		In presence of 200 mg. of titanium	Titanium absent
0.10	4	0.135	0.130
0.50	4	0.77	0.77
1.00	2	0.76	0.76
4.00	0.5	0.83	0.83

* With green filter.

RESULTS—

In Table VI results obtained with the absorptiometric method outlined below are compared with those from a method in which the titanium was precipitated with zinc oxide. Manganese was then estimated in the filtrate by the sodium bismuthate-ferrous sulphate titration or by an absorptiometric method. The direct method was performed in 1 hour.

Table VII shows the results obtained with synthetic mixtures of titanous sulphate and manganese sulphate.

TABLE VI

COMPARISON OF DIRECT ABSORPTIOMETRIC METHOD WITH A SEPARATION METHOD

Material	Manganese found	
	By absorptiometric method, %	By separation method, %
Titanium ABP	0.04	0.03
Titanium - manganese alloy	1.25	1.22
	1.25	1.23

TABLE VII

SYNTHETIC SOLUTIONS CONTAINING 200 MG. OF TITANIUM

Manganese added, mg.	Manganese recovered, mg.
0.25	0.248
0.50	0.498
1.50	1.505
2.50	2.50
3.50	3.50
4.00	3.98

METHOD

REAGENTS—

Sulphuric acid—A solution of 300 ml. of 36 *N* sulphuric acid diluted with water to 1 litre.

Potassium periodate—A solution of 5 g. of potassium periodate in 100 ml. of diluted nitric acid (1 : 4).

Hydrogen peroxide—A 10-volume solution.

Sodium nitrite—A 1 per cent. solution.

Nitric acid—A solution of sp.gr. 1.40.

PROCEDURE—

Transfer 0.2 g. of titanium (containing not more than 4 mg. of manganese) to a 250-ml. squat beaker, add 30 ml. of 30 per cent. sulphuric acid and warm until the reaction has ceased. Add hydrogen peroxide (10-volume solution) dropwise until the red-brown colour of the titanium complex is evident, and then evaporate until colourless and all the titanium is in solution. Cool, add 20 ml. of water and 10 ml. of nitric acid (sp.gr. 1.40); then heat to boiling, and add 10 ml. of potassium periodate solution. Boil the solution for 5 minutes and then cool. Transfer to a 100-ml. standard flask and dilute to volume.

Measure the absorption using a cell of correct size and a green filter of maximum transmission at 5200 Å. Destroy the colour in the remainder of the solution in the flask by dropwise addition of 1 per cent. sodium nitrite solution, and measure the absorption of this "blank."

CALIBRATION—

Manganese solution—A solution of potassium permanganate containing 0.2877 g. per litre gives a solution of which 1 ml. contains 0.05 per cent. of manganese calculated on a sample weight of 0.200 g. This solution is prepared with the usual precautions and standardised against 0.01 N sodium oxalate solution.

Weigh 0.2-g. portions of titanium (manganese-free or of known manganese content) and add to each portion a suitable amount of manganese solution, and treat as in the method.

The range of the method is as follows—

Range, %	Cell length, cm.
0 to 0.25	4
0 to 0.50	2
0 to 1.00	1
0 to 2.00	0.5

The results obtained are within ± 1 per cent. of the manganese content.

REFERENCES

1. Haywood, F. W., and Wood, A. A. R., "Metallurgical Analysis by Means of the Spekker Absorptiometer," Adam Hilger, Ltd., London, 1944.
2. Thornton, W. M., jun., "Titanium," Amer. Chem. Soc. Monograph series No. 33, N.Y. Chemical Catalogue Co., 1927.
3. Snell, F. O., and Snell, C. T., "Colorimetric Methods of Analysis," Chapman & Hall, Ltd., London, 1936, Vol. I, p. 286.
4. Williams, C. H., *Australian Chem. Inst. J. and Proc.*, 1946, **13**, 224.
5. Hough, G. H., *Ind. & Eng. Chem., Anal. Ed.*, 1935, **7**, 408.
6. Guerin, B., private communication.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION
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February, 1950

The Use of Gelatin in the Determination of Silicon in Ferrous Alloys, Especially Silicon-Rich Ferro-Alloys

BY M. H. JENKINS AND J. A. V. WEBB

SYNOPSIS—The precipitation of silica by means of gelatin and its application to silicon determinations on high-silicon alloys is discussed. Two methods have been devised. One involves the boiling of a sulphuric-acid extract of the melt; it gives results that are low, though possibly suitable for plant-operating requirements. The other involves a dehydration procedure prior to the precipitation of silica by gelatin; it is as rapid as the first method and capable of giving a high degree of accuracy.

In order to overcome the drawbacks of the conventional dehydration methods for the determination of silicon in steels, alloys and other materials, numerous workers^{1,2,3,4,5,6} have introduced modifications utilising the fact that colloidal solutions of glue, isinglass, gelatin and related substances cause silica to be precipitated from colloidal solutions of silicic acid. Attempts to apply this principle to silicon-rich ferro-alloys do not appear to be successful to date, and the purpose of this study was to apply it to this type of alloy.

The most thorough investigations to date appear to be those of L. Weiss and H. Sieger³ and K. L. Weiss.⁴ Their papers cover not only the underlying principles, but also optimum experimental conditions, sources of error and application to a variety of materials, chiefly steels of different types. These two papers served as a basis for the work outlined below.

EXPERIMENTAL

The experimental work was divided into three parts, the application of the Weiss method for steels, carbonate fusions of pure silica, and sodium peroxide fusions of ferro-alloys.

METHOD FOR STEELS

Procedure—Dissolve 5 g. of steel in hydrochloric acid and add nitric acid dropwise until the ferrous chloride is oxidised. Adjust the acidity to 20 per cent. or more (by weight) of hydrochloric acid, and adjust the final volume to 100 to 150 ml. Boil for 10 minutes, add 10 ml. of concentrated hydrochloric acid, and adjust the temperature to 60° to 70° C.; add 5 ml. of 2 per cent. gelatin solution dropwise, stirring vigorously all the time and for at least 1 minute after the addition, drawing as much air as possible into the solution. Allow the solution to stand for 5 minutes, dilute to double the volume, and filter. Proceed as in the usual gravimetric method.

Results—The method was tested and the following conclusions were drawn—

(a) For silica (SiO_2) concentrations below about 40 mg. per 100 ml., results tended to be low. Above this concentration, satisfactory results were obtained. With straight carbon steels containing 0.20, 0.29, 0.41, 1.59 and 1.91 per cent. of silicon, values of 0.14, 0.26, 0.41, 1.59 and 1.91 respectively were obtained, while with stainless steels, containing about 12 per cent. of chromium, and 0.12, 0.19, 0.38, 0.39, 0.48 and 0.72 per cent. of silicon, values of 0.07, 0.12, 0.38, 0.33, 0.50 and 0.75 per cent. of silicon were obtained.

(b) For a concentration of 20 per cent. w/w of hydrochloric acid, all results tend to be low and an appreciably higher concentration is advisable. The above results were obtained by using a concentration of 26.5 g. of hydrochloric acid per 100 ml. of solution before boiling.

(c) Other conditions prescribed by Weiss, namely replenishment of boiled-off acid, temperature adjustment and the standing period after gelatin addition were found to be essential. Increasing the standing period did not increase the accuracy of the results.

USE OF SULPHURIC ACID—

Further investigation showed that replacement of part of the hydrochloric acid by sulphuric acid had the advantages that a higher boiling temperature could be obtained, and sulphuric acid is non-volatile and cheap. With a slightly longer standing period, more accurate results for small amounts of silicon were obtained. With 5 g. of sample dissolved in 50 ml. of hydrochloric acid (2 + 1), 50 ml. of sulphuric acid (1 + 1) added before boiling, and 15 ml. of hydrochloric acid after boiling and standing for 10 minutes before dilution, the

following results were obtained: 0.18 per cent. of silicon on a mild steel of 0.20 per cent., and on stainless steels containing 0.12, 0.20, 0.39 per cent. of silicon, values obtained were 0.06, 0.22, 0.41 per cent. of silicon respectively.

ACID-SOLUBLE FERRO-ALLOYS—

The foregoing work provided the basis of a method for determining the silicon in acid-soluble ferro-alloys. Increasing the sulphuric acid concentration further gave better results and the following procedure was therefore adopted.

Procedure—Dissolve 5 g. of alloy in 50 ml. of hydrochloric acid (sp.gr. 1.16). Oxidise dropwise with a minimum of nitric acid. Cool and add 50 ml. of sulphuric acid (5 + 1). Boil for 15 minutes, add 20 ml. of water, and cool to 70° C. Add 15 ml. of a 2 per cent. solution of gelatin dropwise, stirring vigorously all the while and for 1 minute after the addition, allow the solution to stand for 15 minutes, dilute to double the volume, and allow to stand for 10 minutes to permit the precipitate to settle. Filter and proceed as usual. Results obtained by this method (shown in Table II) are slightly low, but are within the limits of accuracy usually required for routine determinations. The amount of silica found in the filtrate is approximately constant, and this may make it possible to use a correction factor.

CARBONATE FUSIONS OF PURE SILICA

Investigation of the carbonate fusions of pure silica, though not exhaustive, gave values for the silica recovery which were very low, when the conditions prescribed by the Weisses and Sieger were adhered to. It was difficult to maintain a sufficiently high acid concentration for gelatin precipitation and at the same time to dissolve the melt. Evaporation of the hydrochloric-acid extract gave rise to a hard crust of silica, which could not be removed by a rubber-tipped rod, on the sides of the beaker; this difficulty was also encountered by the Weisses and Sieger. This crust formed when the solution was boiled with high concentrations of hydrochloric acid; the results obtained were low.

This difficulty did not arise in solutions in sulphuric acid, but the results by adding sulphuric acid to the slightly acid extract of the melt and boiling were still low. Increasing the standing time to as much as 2 hours did not increase the recovery of the silica.

PEROXIDE FUSIONS OF FERROSILICONS AND SILICON-RICH ALLOYS

The same difficulties encountered in the carbonate fusions of pure silica were found when peroxide fusions of ferrosilicons and silicon-rich alloys were investigated, and numerous modifications were applied. Finally, the procedure described below was tested and adopted.

Fusions of the samples in the manner described below and treatment of the acidic extract of the melt by the method as described for acid-soluble alloys, but with doubling of the standing time, gave results which, although low, might be acceptable for rapid industrial analyses. The results obtained by this method are given in Table II; the samples used in testing this and the following method are given in Table I.

TABLE I
DESCRIPTION OF SAMPLES USED

Sample No.	Description
1	U.S.A. National Bureau of Standards, Ferrosilicon 58
2	U.S.A. National Bureau of Standards, Ferrosilicon 59
3	U.S.A. National Bureau of Standards, Ferrochromium 64
4	British Chemical Standard, Ferrochromium 204
5	British Chemical Standard, Steel "J," No. 160
Others	Carefully prepared samples, analysed in replicate by Standard methods of analysis

Better results than those in Table II were, however, obtained by a method which involves a single dehydration with sulphuric acid. A technique of dehydration was evolved which is comparatively rapid, and hardly lengthens the time taken for a determination. Consequently the idea of developing a precipitation method dispensing altogether with dehydration was abandoned.

PROCEDURE—

Mix a convenient weight of finely ground sample with 7 g. of flux in an ingot iron crucible, cover with 2 g. of flux and fuse over a suitable gas flame, observing the usual precautions.

For material containing less than 40 per cent. of silicon, fuse 1 g. of sample with sodium peroxide, and for material containing over 40 per cent. of silicon fuse 0.5 g. of sample with a mixture of equal parts of sodium peroxide and sodium carbonate.

TABLE II
PRECIPITATION OF SILICON WITHOUT PREVIOUS DEHYDRATION

Sample No.	Material	Weight of sample taken, g.	Silicon present, %	Silicon found, %	Error	Silica (SiO ₂) found in filtrate, mg.
1	Ferrosilicon	0.25	75.6	75.77	+ 0.17	*
				75.41	- 0.19	*
				75.60	0.00	1.0
				75.48	- 0.12	2.4
6	Ferrosilicon	0.25	72.59	72.54	- 0.05	*
				72.63	+ 0.04	*
				72.44	- 0.14	0.8
				72.54	- 0.05	0.4
7	Ferrosilicon	0.25	72.47	72.26	- 0.21	0.2
				71.92	- 0.58	5.0
2	Ferrosilicon	0.25	50.00	49.83	- 0.17	*
				49.98	- 0.02	*
				50.0	0.00	nil
				49.61	- 0.39	2.2
				49.98	- 0.02	0.2
8	Ferrosilicon	1.0	16.10	15.98	- 0.12	2.6
9	Ferrosilicon	1.0	12.87	12.80	- 0.07	1.2
10	Silicomanganese	1.0	17.48	17.51	+ 0.03	0.8
				17.30	- 0.18	1.4
				17.23	- 0.15	2.6
11	Silicomanganese	1.0	16.39	16.35	- 0.04	2.0
12	Silichromium	1.0	20.76	20.64	- 0.12	3.4
3	Ferrosilicon	1.5	2.05	2.09	+ 0.04	*
4	Ferrosilicon	1.5	1.01	1.10	+ 0.09	*
14†	Ferromanganese Low carbon	5.0	3.09	3.06	- 0.03	3.2
				3.06	- 0.03	2.4
15†	Ferrosilicon Low carbon	5.0	2.36	2.33	- 0.03	*
				2.33	- 0.03	*
16†	Pig iron	5.0	2.69	2.66	- 0.03	3.6
				2.66	- 0.03	3.2
5†	Carbon steel	5.0	0.09	0.08	- 0.01	*

* Not determined.

† Samples 14, 15, 16 and 5 are acid-soluble materials.

Carefully cool the covered crucible in water and then tap it on a firm, clean, metal surface to loosen the cake. Transfer the melt to a clean nickel or steel plate and remove the adhering melt from the crucible and lid by means of a minimum of hydrochloric acid (1 + 1) and by rubbing with a rubber-tipped rod. Wash the cleanings into a 500-ml. Pyrex Griffin beaker with the minimum of water.

Add 30 ml. of concentrated hydrochloric acid to the beaker, and place in a bath of cold water, preferably cooled with ice; move the cover glass to one side and add the melt from the plate, covering the beaker immediately. When the reaction has subsided, wash the traces of melt still on the plate into the beaker with a few drops of hydrochloric acid and a small quantity of water.

Heat the solution for about 10 minutes on a water-bath, partly cool the solution and add 75 ml. of sulphuric acid (3 + 1). Evaporate until fumes of sulphur trioxide just appear, which occurs readily owing to the continuous evolution of hydrogen chloride from the solution.

Cool the solution, and add 75 ml. of water, followed by 10 ml. of concentrated hydrochloric acid. Heat until all the salts have dissolved.

Cool to 70° C. and add 15 ml. of 2 per cent. gelatin solution dropwise, stirring vigorously for at least 2 minutes. Allow the solution to stand for 30 minutes, dilute with 100 ml. of water, and allow the precipitate to settle for a further 15 minutes. Filter through a Whatman No. 540 filter-paper, applying light suction towards the end of the filtration. Wash the precipitate with dilute (1 per cent.) hydrochloric acid, ignite cautiously at first and finally at 1200° C.; then treat with hydrofluoric acid as usual.

Results obtained by this method are given in Table III.

TABLE III
PRECIPITATION OF SILICA AFTER PRELIMINARY SINGLE DEHYDRATION

Sample No.	Material	Weight of sample, g.	Silicon present, %	Silicon found, %	Error	Silica (SiO ₂) in filtrate, mg.
1	Ferrosilicon	0.5	75.60	75.48	- 0.12	nil
				75.54	- 0.06	nil
6	Ferrosilicon	0.5	72.59	72.61	+ 0.02	nil
				72.52	- 0.07	0.2
		0.25	72.59	72.43	- 0.16	—
				72.61	+ 0.02	—
		72.58	- 0.01	—		
7	Ferrosilicon	0.5	72.47	72.43	- 0.04	—
				72.61	+ 0.14	0.2
				72.44	- 0.03	0.4
2	Ferrosilicon	0.5	50.00	50.10	+ 0.10	nil
				49.83	- 0.17	nil
17	Ferrosilicon	0.5	47.95	47.96	+ 0.01	0.4
				47.92	- 0.03	0.4
		0.25	48.01	+ 0.06	—	
		47.86	- 0.09	—		
8	Ferrosilicon	1.0	16.10	16.05	- 0.05	0.6
				16.16	+ 0.06	nil
9	Ferrosilicon	1.0	12.87	12.92	+ 0.05	0.2
				12.91	+ 0.04	nil
10	Silicomanganese	1.0	17.48	17.46	- 0.02	0.4
				17.41	- 0.07	nil
11	Silicomanganese	1.0	16.39	16.44	+ 0.05	0.2
				16.36	- 0.03	nil
18	Ferrosilicon	1.0	15.63	15.62	- 0.01	0.4
				15.55	- 0.08	1.6

DISCUSSION OF RESULTS

Bearing in mind that (i) Pyrex ware was used for the investigation and (ii) the values for silicon listed on the certificate accompanying U.S.A. National Bureau of Standards ferrosilicon sample No. 58 range from 75.53 to 75.90 and for sample No. 59 from 49.92 to 50.3, the results shown in Table III may be regarded as highly satisfactory. The precision of the method is of practically the same order as the A.S.T.M. method.

According to the U.S.A. National Bureau of Standards (see analysis certificate for sample No. 58), 1.0 to 1.5 mg. of silica are left in the filtrate of a peroxide fusion after two dehydrations with sulphuric acid, and 0.6 to 1.0 mg. after two dehydrations with hydrochloric acid. The figures in the last column of Table III show that the proposed method leaves much less silica unprecipitated.

In spite of contrary claims by previous workers, the precipitation of silica by gelatin does not appear to be quantitative within a reasonable period of time, though complete precipitation may be attained for small amounts of silicon. For larger amounts the error is considerably higher and therefore the dehydration method must be used.

Thanks are due to the management of African Metals Corporation, Ferro-Alloys Works, Vereeniging, for permission to publish this paper.

REFERENCES

1. Tananaev, N. A., and Bichkov, M. K., *Zeit. Anal. Chem.*, 1935, **103**, 349-53; also *Zavod. Lab.*, 1935, 648-50.
2. Tananaev, N. V., *Zavod. Lab.*, 1946, **12**, 248-49.
3. Weiss, L., and Sieger, H., *Zeit. Anal. Chem.*, 1940, **119**, 245-80.
4. Weiss, K. L., *Arch. Eisenhüttenw.*, 1941, **15**, 13-18.
5. Spronk, S. J. H., *Chem. Weekblad*, 1947, **43**, 259-64.
6. Lundgren, P., and Thorn, N., *Svensk. Farm. Tid.*, 1948, **52**, 1-4.

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February, 1950

Sodium Peroxide Decomposition of Minerals in Platinum Vessels

By T. A. RAFTER

SYNOPSIS—It is shown that minerals resistant to decomposition by the usual methods can be decomposed easily and completely at comparatively low temperatures by means of sodium peroxide without the slightest attack on platinum vessels and with insignificant attack on iron or nickel vessels. Thermal analyses and gas-evolution experiments were made with several minerals as a preliminary to more detailed study of the mechanism of peroxide decomposition.

THAT sodium peroxide is one of the most powerful decomposing agents for minerals is well known. What does not appear to be so well known is the very low temperature required for the decomposition. In the past, iron or nickel crucibles have been used for peroxide fusions, and platinum avoided on account of severe attack. Work carried out in conjunction with Seelye¹ established the fact that sodium-peroxide decompositions of the most resistant minerals could be made in platinum vessels without the slightest attack on the vessels.

The experiments described in this paper were devised to determine the temperature of decomposition and to study the gases evolved during the reaction.

EXPERIMENTAL

If mixed with sodium peroxide in a platinum crucible and heated for 7 minutes in an electric muffle maintained at $480^{\circ} \pm 20^{\circ} \text{C.}$, zircon, one of the most resistant minerals, was rendered completely soluble in nitric acid.

Many decompositions have been made in platinum crucibles and basins, without loss in weight of the reaction vessels, provided that the temperature was kept below 540°C. , and such easily oxidisable materials as sulphides were avoided. At these low temperatures the attack of peroxide on iron or nickel vessels is also insignificant. A nickel basin weighing 51 g., after seven decompositions of 10 g. of zircon with 25 to 30 g. of sodium peroxide, lost 0.1 g. Many minerals can be decomposed at a temperature 200°C. lower than that required for zircon—with consequently even less attack on the vessel.

This peroxide decomposition has enabled every mineral that has been examined to be brought quickly and cleanly into solution. With osmiridium, however, four successive decompositions were required.

The experimental details for the peroxide-frit decomposition taken from a paper written by the author and Seelye² are given below.

PROCEDURE—

Particle size—Grind all samples to pass a No. 240 B.S.S. sieve. Fine grinding is essential for a 99 to 100 per cent. decomposition at the first attempt. If coarse material is used, a second frit may be necessary.

Take a convenient amount of material (0.2 to 1 g.) in a weighed 30-ml. platinum crucible and mix with 1.2 to 3.0 g. of sodium peroxide. Place the crucible (covered if necessary) on a vitreosil plate well inside an electric muffle next to the pyrometer, the point of which rests on the plate, and leave for exactly 7 minutes. A number of decompositions can be done at the same time. Keep the temperature at $480^{\circ} \pm 10^{\circ} \text{C.}$ for the final 5 minutes.

Whether after disintegration of the cake in water the solution is filtered or immediately taken up in nitric acid depends upon the nature of the mineral and the sequence of chemical operations to be followed. If the digested cake is to be acidified, it is advisable to add the acid rapidly to the cold alkaline solution; this avoids the precipitation of insoluble acids, which occurs if the neutral point is approached slowly. After acidification and filtration, any unattacked mineral can be recovered and re-treated. If the aqueous extract of the melt is filtered to remove soluble sodium salts and the residue treated with diluted nitric acid (1 + 3), any undecomposed mineral remains on the filter-paper.

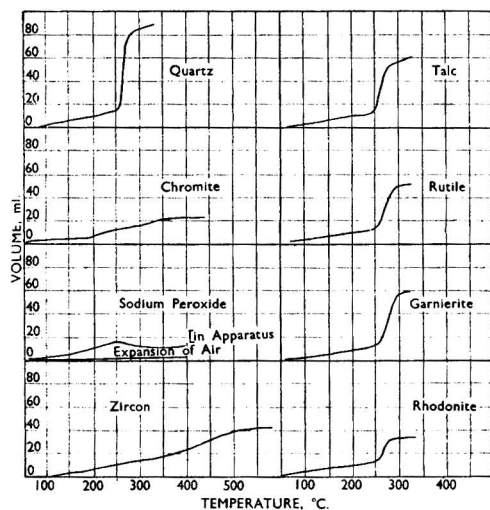


Fig. 1. Temperature-gas evolution curves for the decomposition of minerals by sodium peroxide.

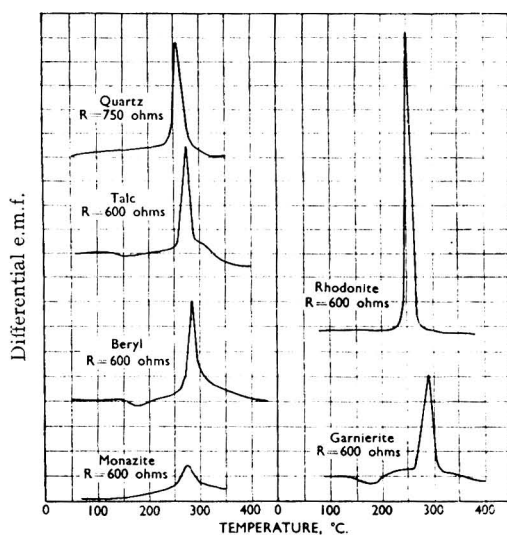


Fig. 2. Thermal analysis curves for the decomposition of minerals by sodium peroxide.

QUALITY OF SODIUM PEROXIDE USED

This paper describes an examination of the use of sodium peroxide as a reagent for decomposing resistant minerals. The sodium peroxide used was taken from one tin of AnalaR brand. It was found that various methods of analysis of the peroxide gave different results. The iodimetric method described in "AnalaR Standards for Laboratory Chemicals"³ was found to be very slow even when catalysed by sodium tungstate, and gave a yield of 82 per cent. of peroxide. The method given by Thorpe,⁴ in which loss of oxygen is avoided by mixing the powder with boric acid, acidifying with sulphuric acid and titrating with potassium permanganate, gave a yield of 92 per cent. of peroxide. A gas-evolution method is also described by Thorpe.⁴ The gas evolved on acidifying with sulphuric acid containing 2 drops of a saturated solution of cobalt nitrate is collected over caustic potash. This method gave a yield of 98.3 per cent. of peroxide. On analysis of the gas, it was found that 2 ml. of nitrogen was mixed with the oxygen liberated from 1 g. of peroxide. The peroxide content after correction for nitrogen was 95.6 per cent. The content of peroxide in the sample was probably 92 to 96 per cent.

As work is described below on the evolution of oxygen when various minerals were heated with peroxide, it was necessary to find the amount of gas evolved when the sample of sodium peroxide is heated alone, in order to apply a correction for it. The peroxide was heated in a platinum Lawrence Smith alkali tube as described later, and the amounts of gases evolved are shown in Table I.

TABLE I
GAS EVOLVED FROM SAMPLES OF SODIUM PEROXIDE

Weight of Na ₂ O ₂ taken, g.	Temperature, °C.	Total volume of gas evolved per g. of Na ₂ O ₂ , ml. at N.T.P.	Volume of oxygen per g. of Na ₂ O ₂ , ml. at N.T.P.	Volume of nitrogen per g. of Na ₂ O ₂ , ml. at N.T.P.
1	200	4.48	2.36	2.12
2	200	4.28	2.93	1.34
1	300	4.24	3.36	0.88
2	300	3.22	3.14	0.15
1	400	2.75	2.16	0.59
2	400	2.68	2.65	0.05

From these results it appears that some of the nitrogen evolved at lower temperatures is reabsorbed at higher temperatures.

GAS-EVOLUTION ANALYSIS

To study the temperature of decomposition of minerals by sodium peroxide and the volume of gas evolved, the Gooch platinum apparatus for the determination of moisture in rocks was first used, but was later replaced by a Lawrence Smith alkali tube and rubber stopper. The rubber stopper was kept cool by cold water run through a few turns of copper tubing. A short glass tube connected the platinum tube to a gas-collecting burette filled with 10 per cent. caustic potash solution. The platinum tube was heated in a copper block by a small vertical electric furnace. The temperature of the block was recorded.

The copper block was heated at a uniform rate of 5° C. per minute and the volume of gas recorded. Typical gas-evolution curves are shown in Fig. 1.

About 0.2 g. of mineral was used, mixed with about 0.6 g. of sodium peroxide, great care being taken to avoid access of moisture.

The curves of Fig. 1 indicate that quartz and talc decompose very easily at a temperature between 260° and 270° C. with evolution of a considerable amount of oxygen; from the chromite curve it appears that in spite of complete decomposition little or no oxygen is evolved; rutile decomposes at the same temperature as talc; zircon is attacked much more slowly over a considerable range of temperature. The curve for sodium peroxide indicates that comparatively little decomposition takes place when sodium peroxide alone is heated.

Table II indicates the volume of gas evolved, corrected to N.T.P., for the weights of the various minerals shown. The gas is mainly oxygen, but a correction has to be applied for a small volume of inert gas (presumably nitrogen) liberated on the decomposition of sodium peroxide, and not reabsorbed as it is when peroxide is heated alone.

The following equations have been used to calculate the theoretical amounts of oxygen evolved—

Mineral	Equation
1. Quartz ..	$\text{SiO}_2 + 2\text{Na}_2\text{O}_2 = \text{Na}_4\text{SiO}_4 + \text{O}_2$
2. Talc ..	$3\text{MgSiO}_3 \cdot \text{H}_2\text{SiO}_3 + 8\text{Na}_2\text{O}_2 = 3\text{MgO} + 4\text{Na}_4\text{SiO}_4 + \text{H}_2\text{O} + 4\text{O}_2$
3. Rhodonite ..	$2\text{MnSiO}_3 + 6\text{Na}_2\text{O}_2 = 2\text{Na}_4\text{SiO}_4 + 2\text{Na}_2\text{MnO}_4 + \text{O}_2$
4. Beryl ..	$3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 + 16\text{Na}_2\text{O}_2 = 6\text{Na}_4\text{SiO}_4 + 3\text{Na}_2\text{BeO}_2 + 2\text{NaAlO}_2 + 8\text{O}_2$
5. Rutile ..	$\text{TiO}_2 + 2\text{Na}_2\text{O}_2 = \text{Na}_4\text{TiO}_4 + \text{O}_2$
6. Garnierite ..	<i>Sample of indefinite composition</i>
7. Chromite ..	$2(\text{FeO} \cdot \text{Cr}_2\text{O}_3) + 7\text{Na}_2\text{O}_2 = 2\text{Na}_3\text{FeO}_3 + 4\text{Na}_2\text{CrO}_4$

X-ray studies or optical examinations would be necessary to verify the equations for the reactions given above. X-ray powder photographs were taken of the frit remaining when the calculated amounts of quartz and peroxide in accordance with equation 1 were used. The product was devoid of quartz and peroxide, and was not metasilicate, but as no A.S.T.M. diffraction-data card for the orthosilicate was available its presence could not be checked.

TABLE II
VOLUMES OF GAS EVOLVED

Mineral	Weight taken, g.	Weight of Na ₂ O ₂ taken, g.	Temperature of decomposition, ° C.	Gas evolved, ml. at N.T.P.	Theoretical volume, ml. at N.T.P.	Difference, ml.
1. Quartz ..	0.183	0.63	260	72.1	68.2	3.9
2. Talc ..	0.193	0.59	270	51.7	45.5	6.2
3. Rhodonite ..	0.197	0.60	270	24.5	16.9	7.6
4. Beryl ..	0.198	0.64	270	70.5	65.9	4.6
5. Rutile ..	0.144	0.61	270	46.0	40.4	5.6
6. Garnierite ..	0.191	0.60	270	48.9	—	—
7. Chromite ..	0.199	0.61	270	2.7	nil	2.7

The volume of nitrogen evolved during the decompositions summarised in Table II was found by analysis to average 2.9 ml. From the data given in the table and from the relevant equations it was calculated that the volume of oxygen produced by the action of heat on the sodium peroxide in excess of that required to react with the mineral would average about 1.0 ml. On average, a total correction of 3.9 ml. should, therefore, be deducted from the volume of gas evolved as shown in Table II. This correction considerably reduces the difference between the experimental and the theoretical volume of gas evolved. With some of the minerals, *e.g.*, rhodonite, the difference is partly due to the presence of impurities.

The table shows a fairly good correspondence between actual and theoretical evolutions of oxygen, and in conjunction with the gas-evolution curves indicates that the reactions are not necessarily dependent on oxidation—indeed the most vigorous, that with quartz, is due to combination only.

DIFFERENTIAL THERMAL ANALYSIS

The encouraging results obtained by the gas-evolution experiments led to an attempt to study the nature of the reaction by differential thermal analysis. An apparatus for differential thermal analysis with automatic photographic recording was used. As the chromel-alumel thermocouple used for the thermal analysis of clays was found to be too sensitive for the decomposition experiments, it was replaced by one of platinum and platinum-rhodium.

The copper block used for holding the platinum crucibles during the decomposition was 2.5 cm. thick. It had two holes to receive the platinum micro-crucibles, a third hole to receive a thermocouple, and a fourth tapped hole to facilitate removal of the block from the furnace by means of a threaded rod. One crucible held the mixture of mineral and peroxide, while the other held the alumina used as the reference material.

The mineral was ground to pass a No. 320 B.S.S. sieve, and 0.2 g. was intimately mixed with 0.45 to 0.6 g. of sodium peroxide. After each experiment the completeness of the decomposition was checked by weighing any residue after solution of the reaction products in dilute acid.

The curves obtained for the less resistant minerals (quartz, talc, rhodonite) are shown in Fig. 2, and those for the more resistant minerals (chromite, rutile, zircon) in Fig. 3. These curves show that the decomposition of most silicates and other minerals by sodium peroxide takes place at a temperature between 250° and 300° C. The reaction for the less resistant minerals is strongly exothermic, and only with the more resistant minerals (*e.g.*, zircon) are temperatures higher than 300° C. necessary for complete decomposition. Before the exothermic peak for the minerals chromite, rutile and zircon, an endothermic peak appears, more developed in some instances than in others.

The significance of this peak can be understood by consideration of the thermal analysis curve for sodium peroxide reproduced in Fig. 4. The curve has been redrawn from that experimentally obtained, in order to have the cooling curve on the same temperature scale as the heating curve, and to show a uniform rate of cooling, which could not be obtained in practice.

At the temperature required for the decomposition of most minerals, sodium peroxide undergoes an endothermic change. Another endothermic peak occurs between 400° and 500° C. in the region of the reported melting-point of peroxide. The cooling curve shows that the changes are reversible, exothermic peaks appearing at temperatures approximately the same as those of the endothermic peaks of the heating curve.

Characteristic colour changes and other alterations were noted during the heating of the peroxide, and these changes were reversed on cooling.

At about 260°C ., fresh AnalaR sodium peroxide undergoes an endothermic change accompanied by incipient fusing or fritting of the particles. Whether this incipient fusion is characteristic of pure sodium peroxide has not been determined. It is probable (see later) that traces of sodium hydroxide present or formed by absorption of moisture during the handling and heating of the powder result in the formation of a low melting point mixture, as the reported melting-point of sodium hydroxide is 318°C .

The thermal analysis curves suggest that when peroxide reaches a temperature of $260^{\circ} \pm 10^{\circ}\text{C}$. it becomes reactive with most minerals with which it is in intimate contact. With chromite and rutile, reaction takes place only after a portion of the endothermic peak

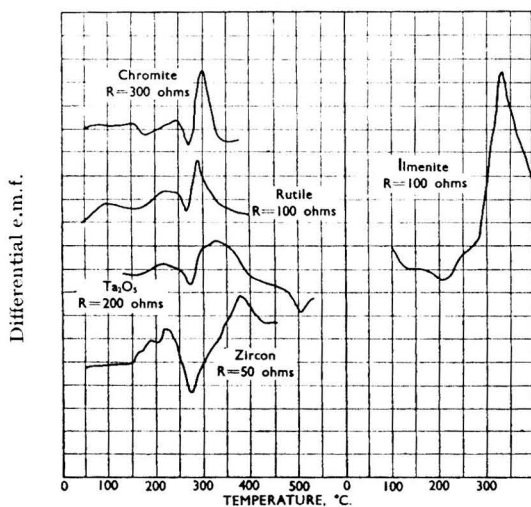


Fig. 3. Thermal analysis curves for the decomposition of minerals by sodium peroxide.

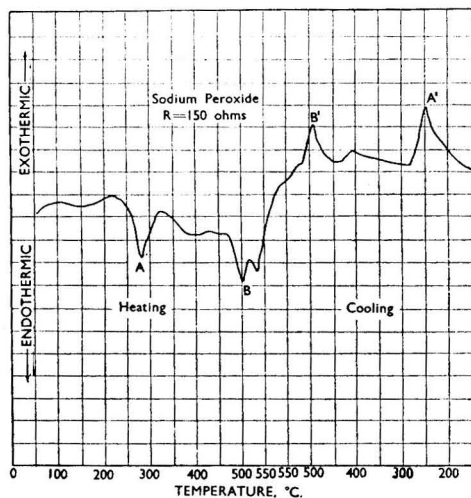


Fig. 4. Thermal analysis curve of sodium peroxide.

associated with peroxide appears, the depth of this peak being an approximate index of the resistance of the mineral. With zircon there appears to be a slight break between the endothermic peak and the exothermic peak accompanying the decomposition. The curve for tantalum oxide has been included, as this decomposition may in the future play an important part in the analytical chemistry of the earth-acid elements.

CALCULATION OF THE TEMPERATURE RISE DURING DECOMPOSITION—

A galvanometer connected to the thermocouples in the heating block was calibrated in millivolts per cm. and from specially constructed tables the approximate temperature rise during the reaction was obtained (see Table III).

Table III shows that peroxide attacks easily-decomposable minerals with the evolution of a considerable amount of heat. If an unknown substance is to be decomposed by peroxide in platinum, the safest procedure is to commence heating at 200°C . and slowly increase the temperature. The heat evolved at the moment of decomposition will then be unable to raise the temperature of the platinum to that at which it is attacked by peroxide. From the figures for the percentage decomposed, it can be seen that complete decomposition has not been obtained for rutile, chromite or zircon. Two results have been included for chromite. In each case the temperature rise at the peak temperature was the same, although in the first experiment 69 per cent. was decomposed and in the second, 98 per cent. The difference between these results was due to the temperature at which the thermal analysis was stopped. In (a) the reaction stopped at 350°C ., in (b) at 450°C . Up to 350°C ., the thermal analysis curves were almost identical, but for (b) further exothermic peaks appeared at temperatures above 350°C ., indicating additional attack.

To study the effect of longer times and higher temperatures on the decomposition, rutile and peroxide were heated to 300° and 350° C. and held at these temperatures for a definite time. The results are given in Table IV.

TABLE III
TEMPERATURE DURING REACTION

Mineral	Peak temperature, ° C.	Temperature rise, ° C.	Mineral decomposed, %
Quartz	263	191	100
Talc	266	65	100
Rhodonite	250	165	100
Beryl	283	62	98
Garnierite	284	56	100
Rutile	286	7	68
Chromite (a)	297	24	69
(b)	294	24	98
Monazite	271	15	—
Ilmenite	279	25	94
Zircon	385	10	65
SODIUM PEROXIDE			
Heating A	279	-11	
B	492	-8	
Cooling B'	498	+8	
A'	254	+11	

Table IV shows that to decompose rutile completely it would be necessary to heat at 350° C. for 40 to 45 minutes. The shape of the thermal analysis curves for these decompositions has not been reproduced for this paper. The curves for heating to 350° C. were very similar, but during the time that the temperature was held constant, indefinite exothermic peaks occurred at nearly regular intervals. The table shows that the peak

TABLE IV
EFFECT OF TIME AND TEMPERATURE ON DECOMPOSITION

Run No.	Peak temperature, ° C.	Temperature rise, ° C.	Percentage decomposed,	Remarks
28	286	7	68	Heated to 350° C. in 30 minutes
30	291	7.5	74	Heated to 300° C. in 30 minutes and held for 30 minutes
31	285	11	93	Heated to 350° C. in 36 minutes and held for 30 minutes
32	283	7	98	Heated to 350° C. in 40 minutes and held for 40 minutes

temperatures and the temperature rises are reproducible with reasonable accuracy. The temperature rise in run 31 appears to be high, but this was because of the difficulty in determination of the base of the exothermic peak. At the peak temperature, 70 per cent. of the mineral is decomposed. The remaining 30 per cent. can be attacked at a higher temperature or in longer time at peak temperature. Similar experiments were carried out with zircon, and, as expected, even higher temperatures or longer times are required for a 70 per cent. decomposition.

X-RAY EXAMINATION—

In an endeavour to correlate any change in crystal structure with the initiation of decomposition by peroxide, powder X-ray photographs were taken of peroxide powder and of the fritted cake obtained after heating the powder to 500° C. and cooling. No change in crystal structure could be detected. The thermal analysis curve for sodium peroxide indicates that no permanent change in crystal structure could be expected, since any change that takes place during heating is completely reversed on cooling.

MICROSCOPIC EXAMINATION—

Minute amounts of peroxide were heated in a platinum dish inserted in a copper block and covered with a glass slide. Any changes that occurred were observed through a microscope. The minute specks liquefied at about 260° C. If larger amounts of peroxide are taken, fritting can be observed, but no visible melting occurs.

THE NATURE OF THE PEROXIDE DECOMPOSITION

The lower temperature peak, A, in the thermal analysis curve for sodium peroxide (Fig. 4) can be attributed to the melting of a small amount of sodium hydroxide present as impurity in the peroxide. The melting point of sodium hydroxide is 318° C., but the fact that the heat change occurs at 280° C. is accounted for by the lowering of the melting point because of the solubility in the melt of a small amount of sodium peroxide or of impurities that may be present.

The upper temperature peak, B, on the thermal analysis curve is apparently due to the heat change at the melting point of sodium peroxide. According to Centnerszwer and Blumenthal⁵ the melting point of sodium peroxide is 460° C. The present work gives the melting point as 495° C., and this should be accurate to within 5° C. It is, of course, the value for the particular sample, containing at least 5 per cent. of impurities; but impurities should make the melting point lower than that of pure material.

From the fact that there are indications of smaller intermediate peaks as well as the two major peaks at 280° and 495° C., it appears that further work is desirable on the phase diagram for mixtures of sodium peroxide with impurities occurring in the commercial product.

It is probably the presence of the liquid phase in the mixture, as shown both by microscopic examination and by the lower temperature peak, A, of the curve, which enables the reaction to proceed rapidly. This does not explain why the peroxide is so much more reactive than the hydroxide at low temperatures, although it suggests that the cause may be the solution of some of the peroxide in fused hydroxide.

APPLICATION OF THE PEROXIDE DECOMPOSITION AT LOW TEMPERATURES

It has been shown that the most resistant minerals can be readily brought into solution by a peroxide frit in platinum vessels without any attack on the reaction vessel. This method of decomposition should prove of great help to the analytical chemist, especially in the analysis of the earth-acid and rare-earth minerals. Schoeller, in his treatise on the earth-acids, does not favour the use of alkali fusions owing to platinum contamination. We have found at the Dominion Laboratory that the peroxide frit brings completely into solution tantalum oxide and the few tantalum minerals that are available in New Zealand. The fritted cake dissolves completely in cold water. If the solution is acidified with tartaric acid it remains clear indefinitely, and can be used as the starting-point for the separation of the earth-acid elements. Preliminary experiments indicate that, by taking advantage of the differences in stability of the persalts of the earth-acids, it is possible to reduce the amount of niobium in reagent samples of tantalum pentoxide, or of titanium in supposedly chemically pure niobium metal.

In the industrial field, if peroxide could be reduced in price, its ease in handling, its lack of corrosiveness, and the ready solubility of the reaction products after the peroxide frit could greatly simplify many existing metallurgical processes, especially for the more valuable elements.

The writer wishes to express his appreciation to Mr. F. J. T. Grigg, Director of the Dominion Laboratory, Wellington, New Zealand, for permission to publish this paper; to Mr. F. T. Seelye for his active interest and advice; to Mr. W. Vose, Director of the New Zealand Pottery and Ceramic Research Association, for advice on the practical application of the peroxide decomposition, and for the use of the Research Association's facilities; to Mr. I. McDowall under whose directions the thermal analyses were made; to Mr. J. D. Butler, who performed most of the gas evolution experiments and analyses of the sodium peroxide; and to Mr. R. J. Munster, who carried out the X-ray work.

REFERENCES

1. Seelye, F. T., and Rafter, T. A., *Nature*, 1950, **165**, 317.
2. ———, ———, Report of Dominion Laboratory, Rock and Mineral Section (unpublished), 1948.
3. "AnalaR Standards for Laboratory Chemicals," British Drug Houses Ltd., and Hopkin & Williams Ltd., London, 1944, p. 190.
4. Thorpe, E., "Dictionary of Applied Chemistry," Vol. 6, Longmans, Green & Co., Ltd., London, 1926, p. 242.
5. Centnerszwer, M., and Blumenthal, M., *Bull. Acad. Polon. Sc. Letter*, 1933, (A), 502; "Landolt - Bornstein Phys. Chem. Tabellen," Ed. III, 325, Berlin, 1935.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH
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WELLINGTON, NEW ZEALAND

April, 1950

Titrimetric Determination of Ethylene

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SYNOPSIS—The determination of ethylene in gas mixtures that contain no other unsaturated compounds, by shaking with excess of bromine in acetic acid, and titrating the unreacted bromine, is described. The method is simple and reliable, and gives results accurate to ± 0.02 per cent.

A METHOD is described for determining the amount of ethylene in gas mixtures containing up to about 7 per cent. of ethylene with an accuracy of ± 0.02 per cent. The usual gasometric methods, such as those employing the Bone and Wheeler apparatus, can be relied upon at best to ± 0.1 per cent., and the Orsat apparatus only to ± 0.2 per cent. A method was devised which was found to be simple and reliable in operation, capable of being used by the average laboratory assistant, and which gave the desired accuracy. Of the usual gases met with in normal gas analyses, only other unsaturated compounds can interfere. The method depends on the determination of the unreacted bromine remaining after a known volume of gas mixture has been shaken with an excess of bromine solution, under specified conditions.

METHOD

REAGENTS—

Sodium thiosulphate—0.1 N, standardised in the usual way.

Potassium iodide—10 per cent. solution.

Starch solution—1 per cent. solution.

Saturated brine—A solution of commercial salt, boiled and filtered.

Bromine in acetic acid—5 g. of potassium bromide, 1 ml. of bromine, 300 ml. of acetic acid.

All the reagents (except the brine) were prepared from A.R. grade chemicals.

APPARATUS—

The apparatus is shown in Fig. 1. It consists of two bulbs separated by a tap, with a further tap at each of the other ends of the two bulbs, and a funnel attached to the tap of the small bulb. The volume of the smaller bulb is about 100 ml. and that of the larger bulb 1 litre. The two taps connected to the smaller bulb are of 8 mm. bore.

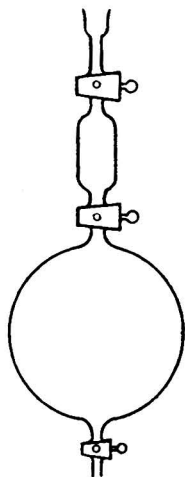


Fig. 1.

PROCEDURE—

The larger bulb is filled with saturated salt solution through the funnel and the small bulb. The middle tap is then closed, and the apparatus inverted, and used in the normal

manner of collecting a gas sample. After the sample is taken the tube is returned to the original position, and the temperature in the smaller bulb is measured; the barometric pressure is also read. By using a wide bore tap, it is possible to insert the thermometer through the bore of the tap. It is assumed that the temperature is the same in the two bulbs. The smaller bulb is then thoroughly rinsed out three or four times with distilled water to wash away all trace of brine.

The bromine in acetic acid reagent is then pipetted into the small bulb, the tip of the pipette being made to pass through the bore of the tap. The quantity of reagent taken is 15 ml. per 1 per cent. of ethylene present in the gas; thus for a gas believed to contain something of the order of 5 per cent. of ethylene, 75 ml. of reagent solution is used. The reagent is conveniently blown into the pipette by means of a blow-ball. No reagent should remain adhering to the funnel or the tap of the bulb, but if any does so, it should be washed in with not more than 1 ml. of distilled water. The tap is then closed.

The middle tap is then opened and the apparatus shaken vigorously for 20 minutes. The middle tap is then closed, the upper tap opened and 20 ml. of 10 per cent. potassium iodide added, and washed in with 1 to 2 ml. of water. The upper tap is then closed and the middle tap opened to allow the iodide to run into the larger bulb. The tap is then closed and the apparatus vigorously shaken for a short time and allowed to stand for 5 minutes.

The liquor is then run into a 500-ml. iodine flask, together with five rinsings of distilled water, each of 10 to 20 ml. The iodine solution is then titrated with thiosulphate in the usual way.

A blank determination is carried out in exactly the same way, using 25 ml. of bromine reagent.

CALCULATION OF RESULTS—

Straightforward calculation shows that if

V = Volume of the larger bulb, in litres,

P = Barometric pressure in millimetres of mercury,

T = Temperature of the gas in degrees C.,

F = Factor of the thiosulphate ($\times 0.1 N$),

a = Titration starting with 75 ml. of bromine solution,

b = Blank titration starting with 25 ml. of bromine solution,

$$\text{the ethylene present} = \frac{0.1121}{V} \times (3b - a)F \times \frac{273 + T}{273} \times \frac{760}{P} \text{ per cent.}$$

REACTION CONDITIONS

BROMINE SOLVENT—

The use of carbon tetrachloride as a solvent for bromine was not found to be satisfactory. Owing to the immiscibility of the carbon tetrachloride with water, it would be necessary to add water as well as the 10 per cent. potassium iodide solution, with a greater risk of loss of bromine by vapourisation at this stage.

Methanol and glacial acetic acid both appear to be suitable solvents.¹ Both gave similar results with the same reproducibility, but the stability of the stock methanol solution was inferior, which made it necessary to carry out blank determinations with each analysis. In the case of the glacial acetic acid solution, one or at most two blanks were sufficient for a day's work.

TIME OF REACTION—

In the first study of the conditions, a temperature of 0° to 5° C. was thought to be desirable in order to reduce possible substitution, either of the ethylene itself or of the accompanying saturated hydrocarbons, and the amount of bromine used was 125 per cent. of that equivalent to the ethylene present. Mixtures of known constitution were prepared volumetrically, using pure ethylene obtained by fractionation on the Podbielniak apparatus. The mixtures contained 4 to 5 per cent. of ethylene, about 5 per cent. of oxygen and 10 per cent. of carbon dioxide, the rest being nitrogen. The results obtained in a number of preliminary experiments are shown in Table I.

TABLE I

EFFECT OF TIME ON THE REACTION

Time of shaking, min.	Ethylene present,	Ethylene found,	Error, %
	%	%	
5	4.49	3.87	- 0.62
5	4.76	3.64	- 1.12
7	4.01	3.35	- 0.66
15	4.65	4.51	- 0.14
20	4.67	4.56	- 0.11

TEMPERATURE OF REACTION—

As the reaction was incomplete even in 20 minutes at 0° to 5°, the cooling was omitted, and the reaction studied at room temperature. The results obtained are shown in Table II.

TABLE II

REACTION AT ROOM TEMPERATURE

Ethylene present,	Ethylene found,	Error,
4.05	3.97	- 0.08
3.51	3.51	0.00
4.12	4.03	- 0.09
4.83	4.82	- 0.01

AMOUNT OF REAGENT—

The excess of reagent taken had first been tried at 25 per cent., which seems to have been used in other connections in determinations with bromine and acetic acid.¹ Experiments were carried out using both 25 and 50 per cent. excess of bromine (calculated for a gas containing 5 per cent. of ethylene). The results obtained are shown in Table III.

TABLE III

EFFECT OF AMOUNT OF REAGENT USED

25 per cent. excess bromine			50 per cent. excess bromine		
Ethylene present,	Ethylene found,	Error,	Ethylene present,	Ethylene found,	Error,
%	%	%	%	%	%
4.05	3.97	- 0.08	5.25	5.23	- 0.04
3.51	3.51	0.00	4.94	4.95	+ 0.01
4.83	4.82	- 0.01	2.97	3.00	+ 0.03
5.51	5.29	- 0.22	4.54	4.54	0.00
4.84	4.73	- 0.11	4.83	4.82	- 0.01
4.13	4.03	- 0.10			
Mean error	- 0.09	Mean error	0.00

The second group of five results in Table III shows the desired level of accuracy in the determination.

Attempts were then made to reduce the shaking time to 5 minutes, using the preferred level of 50 per cent. of excess reagent, and a reaction temperature of 20° C. Under these conditions, however, the reaction was incomplete and deficiencies of up to 0.46 per cent. were recorded. Similarly, a determination which was carried out by shaking for 5 minutes and then allowing to stand for 15 minutes also led to a seriously low result.

COMPARISON WITH GASOMETRIC DETERMINATIONS—

Samples of gas containing ethylene in admixture with (mainly) nitrogen, oxygen and carbon dioxide were analysed titrimetrically and gasometrically with the following results—

TABLE IV
COMPARISON OF ETHYLENE DETERMINATIONS BY THREE METHODS

Mixture	Ethylene found, per cent.				
	Bromine method			Orsat, mean value	Bone and Wheeler, mean value
	Individuals		Mean		
I	3.95	3.93	3.94	3.6	4.1
II	3.59	3.63	3.61	3.6	3.8
III	5.66	5.72	5.69	5.9	5.8
IV	5.01	4.97	4.99	5.0	5.2
V	4.53	4.57	4.55	4.4	4.9

FURTHER TESTS—

Further studies of the reproducibility of the method, and comparison of the results with those obtained gasometrically, were carried out on a gas containing about 90 per cent. of methane, and on another gas consisting in the main of methane, hydrogen, carbon monoxide and nitrogen in roughly equal proportions. The results are shown in Table V, the above mixtures being I and II respectively.

TABLE V
FURTHER COMPARISONS WITH GASOMETRIC METHODS

Mixture	Ethylene found, per cent.							
	Bromine method			Orsat		Bone and Wheeler		
	Individuals		Mean	Individuals	Mean			
I	3.81	3.82	3.84	3.82	3.8	3.7	3.75	4.0
II	0.73	0.74	0.74	0.74	0.6	0.5	0.55	—

The authors wish to thank the Directors of the British Oxygen Co., Ltd. for permission to publish this paper.

REFERENCE

1. Morgan, P. W., *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 500.

THE BRITISH OXYGEN COMPANY LIMITED
MORDEN ROAD, LONDON, S.W.19

May, 1950

Determination of Ferrous Iron in Certain Silicates

By F. R. HARRIS

SYNOPSIS—Errors caused by atmospheric oxidation in the determination of ferrous oxide by Densem's method have been reduced to a negligible quantity by (a) modification of the decomposition chamber and (b) by replacing the direct permanganate titration of ferrous iron by an indirect residual titration in which the ferrous iron in the assay solution is oxidised by means of an excess of standard permanganate solution and the excess determined by adding an excess of standard ferrous iron solution, the excess of which is found by titration to a pink end-point by means of standard permanganate solution.

THE major difficulty in determining ferrous oxide in glasses or other silicates is aerial oxidation during decomposition of the glass and in the subsequent titration. Back-titration methods were suggested by Hackl,¹ though he does not appear to have adopted the idea. Hillebrand² showed that in the rapid grinding of small samples aerial oxidation was negligible. Densem³ used Pratt's method for the determination, in which silicates are decomposed in a gently boiling mixture of sulphuric and hydrochloric acids in an atmosphere of carbon dioxide, and found errors due to dissolved oxygen in the reagents, which were minimised by "boiling-out" all the reagents used. He decomposed the silicates by means of a mixture of sulphuric and hydrofluoric acids in a platinum crucible heated on a sand-bath and enclosed in a cylinder of tinned iron covered by a glass funnel to prevent entry of dust.

The author repeated Densem's work, and while confirming his findings, made modifications in his apparatus and technique which constituted improvements (see Fig. 1). These alterations may be summarised as follows—

- (i) Contamination by sand was avoided by replacing the sand-bath by a layer of asbestos fibre, previously extracted with nitric acid and ignited.
- (ii) The tinned-iron vessel was replaced by one of sheet copper.
- (iii) The crucible was covered by a copper lid, suspended by a copper wire passing through the tubular of the funnel, to prevent condensate falling into it.
- (iv) The decomposition mixture was poured into a boiled-out mixture of boric acid and a measured volume of standard permanganate solution, and air expelled by the addition of a small amount of sodium bicarbonate.
- (v) Densem's titration box was improved by adding a sloping base on which to stand the flask. This prevented reflections in the flask.

These modifications, although of a minor nature, reduced the chances of atmospheric oxidation. In the direct titration method careful work is necessary with samples of low iron content, and the longer the time taken for this, the greater the risk of oxidation. This risk is obviated by back-titration.

METHOD

Boric acid of good quality is dissolved in hot water, filtered to remove ferruginous impurities, which cause erratic blanks, and recrystallised. Two hundred millilitres of distilled water and 10 g. of the purified boric acid are boiled, filtered under vacuum, and then boiled for 10 minutes with 10 ml. of concentrated sulphuric acid. The boiling mixture is poured into a 400-ml. round-bottomed flask, a pinch of sodium bicarbonate added and the flask stoppered, cooled and set aside until required. One to two grams of the glass sample are rapidly and finely ground in an agate mortar, weighed (by difference) and added to a cooled decomposition mixture consisting of 10 ml. of 40 per cent. hydrofluoric acid, 30 ml. of water and 5 drops of concentrated sulphuric acid, which has been previously boiled for 5 minutes and cooled in a platinum crucible under carbon dioxide in the decomposition chamber. After adding the sample, the mixture is again boiled in the decomposition chamber, through which passes a rapid stream of washed carbon dioxide from a cylinder. When the decomposition of the sample is complete, the flask containing the boric acid mixture is opened, a pinch of sodium bicarbonate added, and a measured excess of 0.02 or 0.01 *N* permanganate

solution added from a pipette. The contents of the crucible are then rapidly washed into the flask and shaken. A measured excess of 0.1 *N* ferrous ammonium sulphate solution is then added and the mixture titrated back with 0.02 or 0.01 *N* permanganate solution to the usual pink end-point. This is best seen by means of the light-box described by Densem.

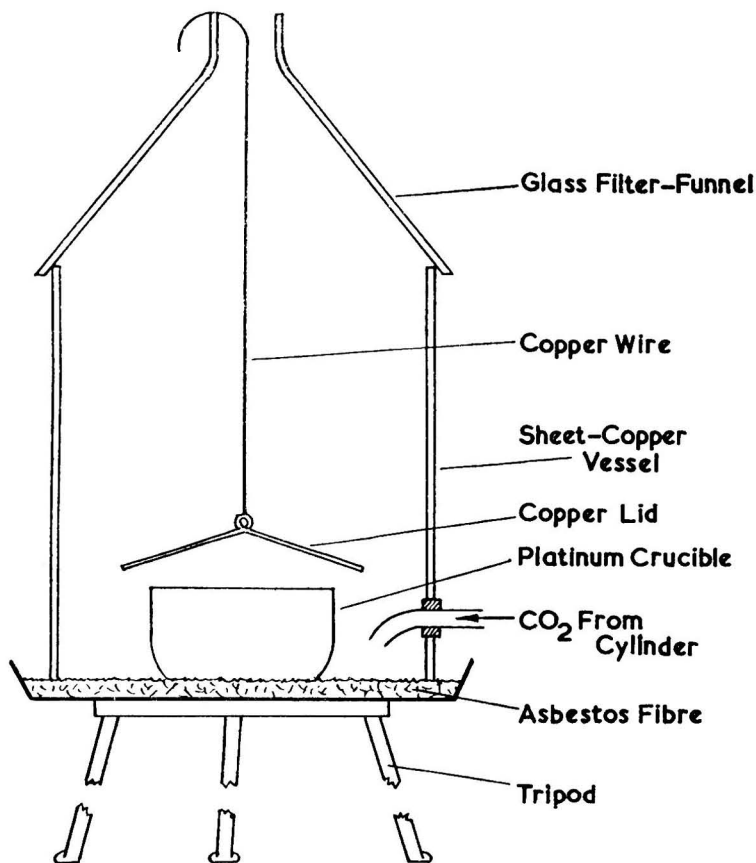


Fig. 1.

Potassium dichromate and ceric sulphate were found to be useless as the oxidant, and internal indicators, such as the diphenylamine derivatives, ferroin, etc., were unsatisfactory. The permanganate end-point was entirely satisfactory.

A blank determination is necessary, but with A.R. quality reagents it is small, usually of the order of 0.2 ml. of 0.02 *N* permanganate, equivalent to about 0.0003 g. of ferrous oxide. The boric acid appeared to be the one suspect material.

RESULTS

The above procedure was tested with known amounts of ferrous salts in place of glass. A comparison of the results by direct titration and by back titration is made in Table I, which shows that there is greater concordance in the replicate results by the recommended procedure than by direct titration, and that the effect of atmospheric oxidation has been reduced.

When the back titration method was applied to a series of simple soda - silica compositions of low iron content there was again concordance in the replicates. This is shown in Table II, which gives the results for a number of glasses containing about 0.1 per cent. of ferrous oxide. Check analyses on some of Densem's glasses are shown in Table III.

TABLE I
COMPARISON OF RESULTS BY DIRECT AND BACK TITRATIONS ON FERROUS OXIDE

FeO added, mg.	Direct titration			Average oxidation, %	Back titration			Average oxidation, %
	FeO found, mg.				FeO found, mg.			
0.1	0.05	0.04	0.06	50	0.09	0.11	0.09	3.0
0.5	0.44	0.38	0.41	18	0.48	0.49	0.48	2.4
1.0	0.94	0.93	0.90	7.7	0.97	0.99	0.98	2.0
2.5	2.08	2.29	2.27	11.0	2.48	2.51	2.50	1.2
5.0	4.94	4.73	4.78	4.0	4.98	4.97	5.00	0.3
10.0	9.74	9.48	9.55	4.0	9.94	9.97	10.04	0.2
25.0	24.30	23.8	24.15	3.7	24.95	24.87	24.90	0.4
50.0	44.9	48.2	47.7	5.4	49.7	49.7	50.05	0.4
100.0	96.8	95.2	95.0	4.7	99.7	99.3	99.8	0.4

TABLE II

RESULTS OF BACK TITRATION METHOD APPLIED TO GLASSES

Glass	A	B	C	D	E
Maximum FeO found, per cent.	0.112	0.119	0.150	0.155	0.182
Minimum FeO found, per cent.	0.099	0.113	0.145	0.151	0.172

TABLE III

COMPARISON OF DIRECT AND BACK TITRATIONS ON GLASSES

Glass FeO, %	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
Densem	0.14	0.23	0.28	0.38	0.43	0.84	1.23
F. R. H.	0.14	0.23	0.29	0.38	0.43	0.84	1.39

In general, agreement is good, and where discrepancies arise it is the new technique which gives the higher (and probably more accurate) figure.

Accuracy of the method for glasses of low iron content having been shown to be satisfactory, the ferrous iron was determined in a series of glasses of high iron content melted by the writer. No comparisons were available for these, but the proximity of the totals to 100 per cent. is a sufficient test of accuracy in glasses of this kind. The results are shown in Table IV.

TABLE IV

DETERMINATIONS OF FERROUS IRON IN GLASSES OF HIGH IRON CONTENT

Glass	SiO ₂ , %	Na ₂ O, %	Total Fe as Fe ₂ O ₃ , %	FeO, %	Fe ₂ O ₃ ≡ FeO, %	True Fe ₂ O ₃ , %	Al ₂ O ₃ , %	Total (a, b, c, d, e), %
	(a)	(b)	(c)	(c)	(d)	(d)	(e)	(e)
1	73.37	24.95	1.44	0.63	0.70	0.74	—	99.69
2	72.39	25.17	2.36	1.26	1.40	0.96	—	99.78
3	71.68	25.05	3.14	1.29	1.43	1.71	—	99.73
4	71.67	24.37	3.94	1.94	2.16	1.78	0.02	99.78
5	72.37	23.38	4.44	2.32	2.58	1.86	0.01	99.84
6	68.76	23.68	7.98	4.98	5.53	2.45	0.02	99.89
7	71.61	21.75	7.10	5.09	5.56	1.45	0.02	99.92
8	67.28	20.80	12.28	4.95	5.50	6.78	0.02	99.84

In these glasses about one half of the iron is in the ferrous state, and under ordinary, direct titration, conditions the time taken for titration would be long and the risk of atmospheric oxidation great. This source of error has been obviated by the method of back titration.

The samples used in this work were prepared for research purposes and their composition differs from that of commercial glasses. It is hoped later to investigate the back-titration method as applied to more complex glasses, including commercial compositions, especially those containing arsenic and manganese.

REFERENCES

- Hackl, O., *Z. anal. Chem.*, 1928, **67**, 197.
- Hillebrand, W. F., *J. Amer. Chem. Soc.*, 1908, **30**, 1120.
- Densem, N., *Glass Review*, 1936, **12**, 64; *J. Soc. Glass Tech.*, 1936, **20**, 303f.

Notes

THE ESTIMATION OF VITAMIN B₁ USING THE FLUORIMETER: THE PREPARATION OF THE STANDARD CURVE

THE method used for the estimation was that recommended in the Medical Research Report published in the *Biochemical Journal* and abstracted in *The Analyst*.¹

It is recommended that the standard curve be obtained by calibrating a series of aneurine standards (oxidised by the same technique as employed for the flour extracts) against the quinine standard. There is a rather serious error in *The Analyst* abstract, where reference is made to a standard quinine solution of 0.01 g. per 100 ml. of 0.1 N sulphuric acid. In the original paper this is the strength of the standard stock solution, and the actual solution used in the fluorimeter cell is a 1 in 100 dilution of this. In the preparation of the graph, it was found that over the approximate range 1.0 to 4.0 $\mu\text{g.}$ of vitamin B₁, the density drum could be accurately read and the points on the curve easily reproduced. In an actual determination it is this part of the curve that is used, but for the "blank" determination an extension of the curve over the range 1.0 to 0.1 $\mu\text{g.}$ is important.

It was decided to prepare from the experimental curve another curve plotting the reciprocal of the antilog of the density as given by the drum reading, against $\mu\text{g.}$ of vitamin B₁. A straight line was obtained passing through the origin. If this straight line is extended to the point 1/antilog (density) = 1.000 and the equivalent $\mu\text{g.}$ of vitamin B₁ read off at this point, then there is no further need for the curve. Any drum reading can be readily converted to $\mu\text{g.}$ of vitamin B₁ by the following formula—

$$\mu\text{g. of vitamin B}_1 = \frac{1}{\text{antilog (density)}} \times \text{constant, C,}$$

where the constant, C = $\mu\text{g.}$ of vitamin B₁ at the point 1/antilog (density) = 1.000. This constant is actually the number of $\mu\text{g.}$ of vitamin B₁ which exhibit a fluorescence equal to the standard quinine fluorescence. Theoretically, using vitamin B₁ itself as the standard fluorescence, if, in an experiment, 5 $\mu\text{g.}$ (say) of vitamin B₁ constituted the standard fluorescence, then without the aid of a curve

$$\mu\text{g. of vitamin B}_1 \text{ in the solution under test} = \frac{1}{\text{antilog (density)}} \times 5$$

It is not recommended that vitamin B₁ itself be used as the standard fluorescence in place of quinine. It should be borne in mind that the accuracy of the standard graph or of the constant, C, depends upon a reproducible quinine standard. Care should be taken when using quinine sulphate B.P. as this substance is very liable to lose its water of crystallisation, and this may lead to errors.

In our own experiments the sample of quinine sulphate used contained 3.7 per cent. of water (*i.e.*, not B.P.) and a constant of 8.0 was obtained from the straight line as deduced from the experimental curve. The formula may be further simplified to

$$\mu\text{g. of vitamin B}_1 = \text{antilog} [\log (\text{constant, C}) \text{ minus (drum reading)}]$$

This method of approach does give a check on the shape of the experimental standard curve and also, if developed as outlined, it simplifies calculation.

REFERENCE

1. "The Vitamin B₁ Content of National Flour and Bread—the Results of Comparative Tests by Various Methods," *Biochem. J.*, 1943, **37**, 433; *Analyst*, 1943, **68**, 379.

CITY ANALYST'S LABORATORY
BIRMINGHAM

F. G. STOCK
March, 1950

DEVICE FOR USE WITH WATER-DRIVEN VACUUM PUMPS TO PREVENT WATER SUCKING BACK INTO APPARATUS

SPORADIC fluctuations in water pressure can cause much annoyance and loss of time when water-driven vacuum pumps are thereby caused to suck back into the apparatus being evacuated. The conventional water-trap is not always an adequate protection, particularly where the apparatus concerned is of any considerable size. For this reason, the pumps in these laboratories have been fitted with the device described below and illustrated in Fig. 1, and have since given entirely satisfactory service.

The apparatus, A, to be evacuated is connected to the capillary system by a length of rubber pressure tubing, B, and the drying tube, C_1 , which can be omitted if desired. We use calcium oxide in C_1 as the drying agent. The tap T_1 serves to release the vacuum in A and the capillary system, water vapour being excluded from the latter by the similar drying tube, C_2 . The manometer, M, gives a continuous indication of the pressure, the lower ends of both M and the tube D being drawn out to an external diameter of approximately 1 mm. The tube D passes through a three-hole rubber bung into the jar E, where it dips into about 1 cm. of mercury. Also passing through the bung are the tap T_2 (which is optional) and the tube P, which is connected to the pump, and whose lower end is protected by the tube H. The latter gives a running fit on P, and is closed at the lower end. It is buoyed up by the mercury and presses on the lower surface of the bung. To prevent this from giving a gas-tight seal, it is necessary to cut a very small notch in the rim with a triangular file.

The apparatus, A, having been evacuated with both taps closed, the vacuum is released as follows—

- (i) Either the pump is turned off or T_2 is opened.
- (ii) T_1 is opened.

The object of this routine is to avoid the violent agitation of the mercury in the jar E which results when T_1 alone is opened, and may cause mercury to be drawn into the pump despite the protection

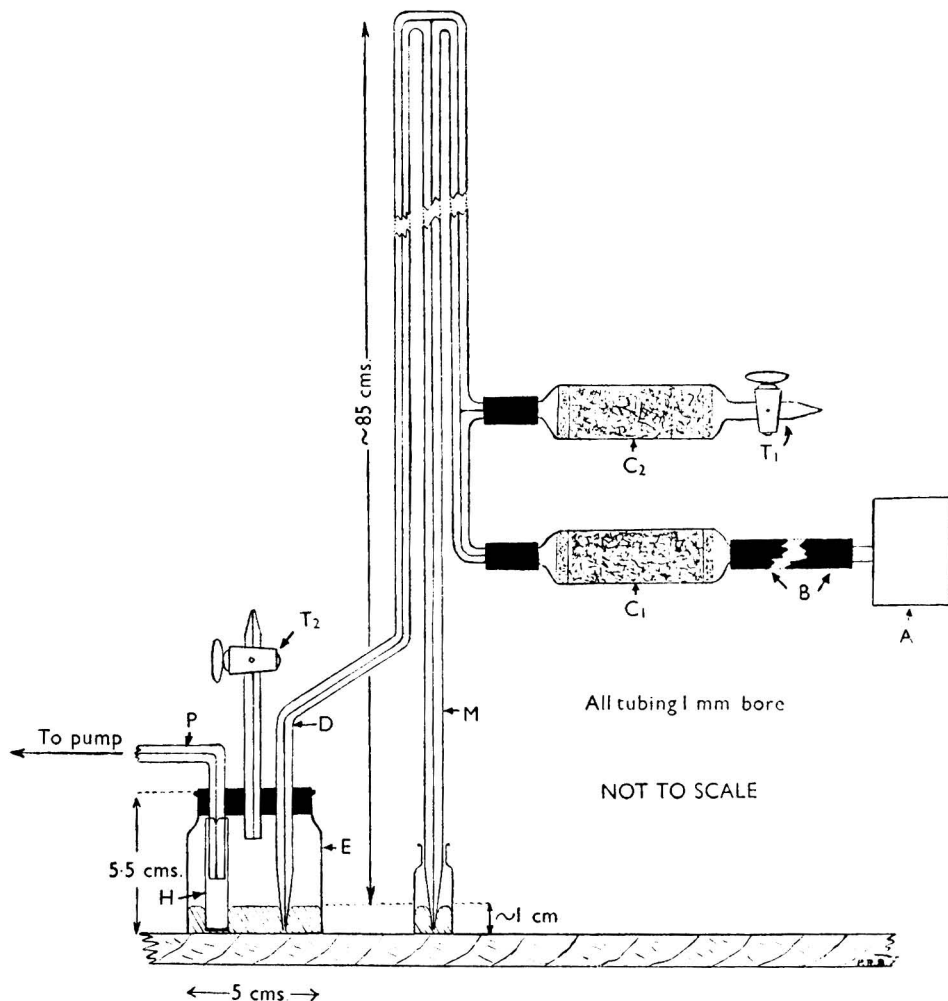


Fig. 1.

afforded by H, especially if the mercury is too deep. The same trouble at the commencement of the evacuation of a large vessel can be controlled by the use of a screw clip on the tube B.

A simplified form of the device may be made in which the manometer M is omitted, when a reading of the pressure at any time may be had by opening T₂. The mercury at once rises in D, and may be measured, whilst the vacuum in the rest of the system is unaffected in the absence of leaks such as dry ground-glass joints in A.

The device described, apart from preventing the entry of liquid water from the pump, offers the additional advantages that water vapour from the pump is excluded from access to the drying agents, and, further, T₁ provides a convenient point at which to inject an inert atmosphere when A has no such point. Excess pressure from a cylinder attached at T₁ is allowed free egress through the pump, in case of accident. Again, the additional volume to be evacuated is minimised, especially when E has filled with water, whereas the usual water-trap is often larger than the apparatus in use.

VIROL LTD.
HANGER LANE
EALING, LONDON, W.5

P. R. BOOTH
April, 1950

A DELICATE TEST FOR CUPRIC AND FERRIC IONS IN AQUEOUS SOLUTION

WHEN potassium hydrogen phthalate and hydrogen peroxide are boiled together in aqueous solution, in the presence of traces of copper or iron salts, the phthalate ion undergoes degradation with the evolution of carbon dioxide and the formation of a strongly brown-coloured colloidal solution. This reaction can be used as the basis of a sensitive test for the two metals. No other metal has been found to give the same series of changes.

PROCEDURE—

Take 100 ml. of the solution under test, add 10 ml. of 0.2 M potassium hydrogen phthalate and 10 ml. of 20-volume hydrogen peroxide, boil, and maintain at 97° to 99° C.

The formation of the brown colour is progressive, and both the time which elapses before the colour is noticeable and the intensity after any given time depend upon the concentration of catalyst. With metal concentrations of 10⁻⁵ M, 2 minutes at 98° C. are sufficient to develop a distinct colour, after which the intensity continues to build up with time. Ten minutes will give a coloration with 10⁻⁶ M solutions, and about an hour gives a detectable colour at 10⁻⁷ M. At concentrations lower than 10⁻⁷ M, some additional reaction between the brown coloration and the excess peroxide interferes with the progressive formation of the colour.

A distinction between copper and iron can be drawn from the fact that fluoride ions completely inhibit the development of the colour with iron catalysis but have no influence on the copper-catalysed reaction. Any reagent that removes the free metal ions from solution is similarly effective, *e.g.*, phosphate ions with iron catalysis.

It is always advisable to carry out blank experiments to check that the reagents are free of catalysts to the desired degree. The water used in these experiments had been distilled twice, the second time from an all-Pyrex glass still. The phthalate had been recrystallised twice from the distilled water and the peroxide was made up by dilution from a stock solution of 100-volume material. With these precautions, the phthalate and peroxide could be boiled together for 6 hours without the slightest formation of the brown colour.

A preliminary study of the reaction has been made, and there is strong evidence to support the view that the metal catalyst is cyclically oxidised and reduced with the liberation of hydroperoxide radical (HO₂), which is then responsible for the degradation of the phthalate and the formation of the brown colour. Other, but not all, benzene carboxylic acid salts give analogous reactions and a great many benzene derivatives undergo severe degradation when in reaction with peroxide and catalyst. Experiments are proceeding on the detailed mechanism of the reaction and it is hoped to publish a full account elsewhere in the near future.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY
UNIVERSITY OF LIVERPOOL

G. A. BOTTOMLEY
April, 1950

A TEST FOR VOLATILE SUBSTANCES PRESENT IN TRACES
APPLICATION TO CYANIDE

By using an inert gas, generated along with the sample in a simple form of Gutzeit apparatus, as a stripping agent and carrier, and a suitable test paper, traces of many volatile substances can be easily and quickly detected and, under appropriate conditions, approximately estimated.

A small flask is fitted with a stopper carrying a short glass tube that has a constriction near the top on which the test paper rests. To prevent spray from reaching the paper the lower end of the tube is loosely plugged with cotton wool, which is changed for each test.

The most suitable paper for the test strips seems to be Whatman No. 54 filter-paper; it is semi-transparent when wet, so that stains show up very clearly, and it can also be dipped into moderately strong acid or alkali, when required, without becoming distorted. It is cut into 4 to 5-mm. wide strips trimmed to a point with an angle of about 60° to enhance sensitiveness. For the detection of traces, this is more sensitive than the modified disc form, because, with a suitable rate of gas production, the stain forms on a much smaller area.

For the detection of traces of cyanide by the method of Gettler and Goldbaum,¹ about 1 inch of the end of the strip is dipped in slightly acidulated 10 per cent. ferrous sulphate solution and dried. Before use, the end is dipped in 10 to 20 per cent. caustic soda solution and the excess removed by momentarily resting it on filter-paper.

The sample and a few grams of zinc of suitable quality are placed in the flask, about 25 ml. of 10 per cent. sulphuric acid solution are added and the stopper with the test paper in place in the tube is inserted. Hydrogen should be evolved freely but not vigorously, the solution being opaque from the presence of innumerable minute bubbles, but not forming a froth; the rate can be regulated by adding copper sulphate solution. The zinc for this test should be practically free from sulphide, since hydrogen sulphide stains the paper black and, if present in any quantity, discharges the cyanide.

The paper is removed and "developed" in 50 per cent. hydrochloric acid to which a little ferric chloride has been added. If cyanide is present the tip of the paper will show a blue stain.

A microgram of hydrocyanic acid is clearly detected in 15 minutes and, with appropriate conditions so that hydrogen is evolved steadily for 45 to 60 minutes, even 0.2 microgram will give a minute stain on the extreme tip of the paper; it is distinctly visible when an unexposed strip is placed in the acid beside it for comparison.

REFERENCE

1. Gettler, D. A., and Goldbaum, L., *Anal. Chem.*, 1947, **19**, 270; Abst., *Analyst*, 1949, **74**, 473.

DEPARTMENT OF CHEMISTRY
ADELAIDE, SOUTH AUSTRALIA

A. R. HICKINBOTHAM
February, 1950

Ministry of Food

STATUTORY INSTRUMENTS*

1950.—No. 1056. **The Food Standards (Preserves) (Amendment) Order, 1950.** Price 2d.

This amending Order, which comes into force

- (a) in respect of sales by the manufacturer of the article, on the 25th day of September, 1950;
- (b) in respect of sales by wholesale and sales by retail, on such dates as the Minister of Food may by Order appoint,

raises the minimum fruit content of certain jams by amending the Food Standards (Preserves) Order, 1944, as amended by S.R. & O., 1944 (No. 842), II, p. 513, S.R. & O., 1946 (Nos. 157 and 1221), II, pp. 26 and 25, and S.I., 1949 (No. 1893), II, p. 9, by substituting the following for Part II of the Schedule—

THE SCHEDULE

PART II

Minimum Fruit Content

Column 1 Description of Jam or Marmalade (Fresh Fruit Standard or Full Fruit Standard)	Column 2 Percentage of Fruit or Vegetables
A.—JAM	
Apple and Blackberry	40 (30/10)
Apple and Blackcurrant	40 (30/10)
Apple and Damson	40 (30/10)
Apple and Plum	40 (30/10)
Apple and Raspberry and/or Loganberry	40 (30/10)
Apple and Strawberry	40 (30/10)
Apple Jelly	40
Apricot	40
Apricot and Peach	40 (20/20)
Bilberry	40
Blackberry (or Bramble) and Blackberry (or Bramble) Seedless or Jelly	38
Blackcurrant and Blackcurrant Jelly	22
Cherry	40
Damson and Damson Jelly	38
Elderberry Jelly and Elderberry Seedless	40
Gooseberry	30
Greengage	38
Loganberry	25
Peach and Mixtures of Peach with Citrus Fruit	40
Pineapple	40
Plum and Plum Jelly	40
Plum and Blackcurrant	40 (30/10)
Plum and Raspberry	40 (30/10)
Plum and Strawberry	40 (30/10)
Quince Jelly	40
Raspberry and Raspberry Seedless or Jelly	25
Raspberry and Gooseberry	30 (15/15)
Raspberry and Loganberry	25 (15/10)
Raspberry and Redcurrant	30 (15/15)
Redcurrant Jelly	35
Rhubarb	40
Rhubarb and Blackberry	40 (30/10)
Rhubarb and Raspberry	40 (30/10)
Strawberry	37½
Strawberry and Gooseberry	35 (17½/17½)
All other Jams	40
B.—MARMALADE†	
	20

NOTE—Where figures in brackets are specified in the second column above in respect of a description of jam containing more than one variety of fruit or vegetables, the first figure denotes the content of the variety of fruit or vegetables first mentioned in such description, and the second figure denotes the total content of the other varieties of fruit or vegetables mentioned in such description.

† For special standard marmalade, see paragraph 5 of Part I of this Schedule.

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

1950.—No. 1061. The Labelling of Food Order, 1950. Price 6d.

This Order substantially re-enacts in a consolidated form the Labelling of Food Order, 1946 (Analyst, 1947, 72, 65) and its amending Orders. Weights and Measures provisions are omitted. Certain new provisions have been introduced, the principal ones being—

- (a) *to provide for the use of the description ginger wine or orange wine for products wholly or partly derived from fruit other than grapes;*
- (b) *to permit the sale of Black Beer and Rum containing not less than 20 per cent. proof spirit;*
- (c) *to permit the sale of alcoholic cordial containing not less than 5 per cent. proof spirit subject to special labelling requirements;*
- (d) *to permit the sale of bitters containing not less than 15 per cent. proof spirit;*
- (e) *to permit the sale of non-alcoholic fruit (or vegetable) juice cocktail containing not less than 80 per cent. undiluted fruit or vegetable juice;*
- (f) *to provide that all liquors for which tonic, restorative or medicinal properties are claimed or which are held out to be beneficial for invalids shall be labelled with a statement indicating the quantity of the ingredients on which the claim is based;*
- (g) *to impose requirements as to the labelling of prepacked concentrated acetic acid;*
- (h) *to prohibit the claiming of tonic properties for any food by reason only that the food contains (a) alcohol, (b) sugars or other carbohydrates, (c) protein or substances prepared by the hydrolysis of protein, or (d) caffeine or other purine derivatives;*
- (i) *to require that pre-packed cheese be labelled in compliance with the provisions of the Order, except as regards declaration of ingredients;*
- (j) *to require that the ingredients of Christmas puddings be specified after the 31st March, 1951;*
- (k) *to permit nuts and synthetic cream to be designated as such when forming an ingredient of some other food; fish to be designated as such when forming an ingredient of fish products, and vine fruits to be designated as such when forming an ingredient of some other food other than a beverage;*
- (l) *to require tomato ketchup, catsup, sauce and relish prepacked for sale as such to be labelled with a declaration of ingredients.*

The provisions of this Order come into force on the 1st of November, 1950, on which date the Labelling of Food Order, 1946, is revoked.

1950.—No. 1239. The Mineral Oil in Food (Amendment) Order, 1950. Price 1d.

This Order, which comes into operation on August 1st, 1950, amends the Mineral Oil in Food Order, 1949 (S.I., 1949, No. 614), so that the prohibition in the principal Order relating to mineral oil in food shall not apply in relation to dried fruit containing not more than 1 part by weight of mineral oil per 100 parts by weight of dried fruit: and makes provision as respects articles of food containing mineral oil by reason of the inclusion therein of dried fruit containing mineral oil.

Dried fruit is defined as prunes, currants, sultanas and raisins.

CIRCULAR MF11/50

This circular, dated 27th June, 1950, gives a list of products that have been approved by the Ministry of Agriculture and Fisheries and the Ministry of Food, under Regulations 26 (6) (a), which provides for the use of oxidising or preservative agents as alternative to scalding with boiling water or steam, in the cleansing of milk tankers, vessels or appliances.

All the products so far approved are solutions of sodium hypochlorite, having a total available chlorine content of between 9 and 12 per cent. w/w, and containing not less than 0.7 per cent. w/w of sodium chlorate, to act as a detector should any sodium hypochlorite solution get into the milk through vessels not being properly rinsed or otherwise, and not more than 2 per cent. w/w of free caustic alkali.

6. Regulation 26 (6) (c) requires that all traces of sodium hypochlorite solution (or of any other oxidising or preservative agent that may in future be approved) used for cleansing purposes, shall be removed from milk tankers, vessels or appliances before they are again brought into contact with milk. Samples of milk should accordingly be taken occasionally for testing for the presence of chlorate where approved sodium hypochlorite solutions are used by the dairy, as a check on compliance with this regulation.

The list of products is as follows—

DEOSAN, CHLOROS, DAIROZON, HYPOSAN, DELSANEX.

British Standards Institution

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and may be obtained on application to the Secretary, Miss D. V. Wilson, 7-8, Idol Lane, London, E.C.3.

- Draft Specifications prepared by Sub-Committee RUC/10/8—Testing of Solid Rubber.
CM(RUC) 2655—Draft B.S. Methods of Testing Raw Rubber and Unvulcanised Rubber (Part 1).
CM(RUC) 2964—Draft B.S. Methods of Mixing and Vulcanising Rubber Test Compounds.
- Draft Specifications prepared by Technical Committee LBC/11—Microchemical Apparatus.
CM(LBC) 3293—Draft B.S. for Weighing Vessels for Microchemical Analysis.
CM(LBC) 3292—Draft B.S. for Crucibles for Microchemical Analysis.
CM(LBC) 3291—Draft B.S. for Combustion Boats and Sheaths for Microchemical Analysis.
- Draft Specification prepared by Sub-Committee PVC/1/5—Red Lead Pigment.
CM(PVC) 3493—Draft Revision of B.S. 217: Red Lead for Paints and Jointing Compounds.
- Draft Specification prepared by Sub-Committee PVC/1/6—White Pigments.
CM(PVC) 3490—Draft Revisions of British Standards for White Pigments.
- Draft Specification prepared by Technical Committee LBC/3—Glassware for Pharmaceutical Purposes.
CM(LBC) 3711—Draft B.S. for Cup or Beaker Measures for Pharmacists.
- Draft Specification prepared by Sub-Committee PVC/1/9—Black Pigments.
CM(PVC) 3556—Draft Revision of B.S. 284, 285, and 286: Black Pigments for Paints.

Reviews

OILS, FATS AND FATTY FOODS—THEIR PRACTICAL EXAMINATION. By K. A. WILLIAMS, B.Sc., Ph.D., F.R.I.C. Third Edition. Pp. ix + 500. London: J. & A. Churchill, Ltd. 1950. Price 63s.

The first edition of this work by Bolton and Revis was published in 1913 under the title, "Fatty Foods—Their Practical Examination." It is not now possible to say whether it satisfied a growing demand or whether by the presentation of a carefully considered selection of methods at a time when—as pointed out by the authors in their preface—"the analysis of oils and fats was both prolific of method and uncertain in result" it focussed attention on an unsatisfactory situation and thereby created the demand, but in any case it was immediately accepted as an invaluable reference book and attained a very wide circulation.

A second edition by Bolton, with the indicative name now altered slightly to "Oils, Fats and Fatty Foods," was published in 1928. This covered much the same ground as its predecessor. A third edition has long since been called for but, as pointed out by Dr. Williams, the second world war effectively interfered and it was not until hostilities ceased that he could turn his attention to this task.

The general method of presentation remains unaltered, although particulars of more recent and proved methods have been added to the older fundamental methods that have stood the test of time; and a number of oils are now described which do not appear in the earlier editions. The section on milk products and vitamins has been extended; and a new feature is that not only are the usual ranges of analytical data and figures for typical specimens given but, in the case of the more important oils and fats, the standard figures of the British Standard Institution, the British Pharmacopoeia and the American Oil Chemists Society (U.S.A.) are also given.

Following on a general introduction covering 11 pages, the next 55 pages are devoted to consideration of methods of sampling and preliminary examination, this being the author's somewhat modest way of referring to descriptions of suitable techniques for the preparation of samples for analysis, the determination of moisture and residual solvents, impurities, metallic contamination, glycerine and glycols, refining tests, rancidity, keeping quality and susceptibility to oxidation, and preservatives. It covers the range of such examination, analytical and physical, as may be necessary for commercial purposes. It is to be noted that it does not start from a sample in a bottle, but rather from a wharf with a barge loaded with oil alongside or from a store where the raw material is stacked in barrels or stored in tanks; it thus surveys the problems so often presented in actual practice. In many ways this chapter on sampling and preliminary examination determines the outstanding character of the book.

The next chapter deals with analytical methods, with full working details, and includes methods officially accepted as standard. Here it is to be noted that Dr. Williams points out in his introduction that he has not covered the whole range of analytical methods used in the investigations of oils and fats, and that many methods not commonly used by him have been excluded. It might possibly have been useful to have added a warning that what is accepted to-day may be abandoned to-morrow and that acceptance of a standard method should not mean the abandonment of critical examination and of personal initiative. The extent of the new matter in this chapter can be assessed from the fact that the 55 pages in the previous edition have now been extended to 86 pages: *inter alia*, melting-point methods and colour assessment, particularly with the aid of modern physical instruments, require six or seven times the earlier space; and new additions include bromine, thiocyanogen, and hydroxyl values, determinations of oxidised acids, linoleic, linolenic and elacostearic acids, ester fractionation, and estimation of monoglycerides and glyceryl esters. As an example of the critical way in which methods are considered in this chapter the section on specific gravity and apparent density may be quoted, where, after the usual details of apparatus and correction for temperature, further information on the effect of and correction for stearine deposition are given, followed by a brief but fully detailed account of the method for calculating the weight of oil in bulk when tanks scales are not available.

Short chapters follow on interpretation of analytical methods with analyses of typical samples, industrial production of vegetable oils and fats, and the manufacture, characteristics and analysis of hydrogenated or hardened oils.

About two-fifths of the book is required for what may be regarded as the analytical section indicated above; the next section of about the same length deals first with butter and margarine, then with animal fats, next with marine animal and fish oils, and finally with over one hundred vegetable oils and fats. As with the earlier editions, the sources, characteristics and analytical data of the various oils and fats are given, and as these include many new additions the unique value of this section as a reference book has been very substantially increased.

The final section deals with cooking fats and lard substitutes; cocoa, chocolate and milk chocolate; animal feeding stuffs; milk and milk products; and a dissertation of 8 pages on the nutritive value of edible oils and fats.

Dr. Williams is to be heartily congratulated not only on his comprehensive and thorough revision of the original work, and on the additional data that bring the book up to date, but also on the inclusion of so much new and valuable information based on his own extensive commercial experience. One effect of this is that the sub-title reference to the practical examination of fatty foods takes on a new meaning. The methods as set out are, of course, practical as any other analytical methods are practical, but the issue of this book is rather in effect the practical examination of the results of analysis, a somewhat different matter.

GEORGE TAYLOR

AN ADVANCED TREATISE ON PHYSICAL CHEMISTRY. By J. R. PARTINGTON, M.B.E., D.Sc.
Volume I: Fundamental Principles. The Properties of Gases. Pp. xlii + 943. London:
Longmans, Green & Co. 1949. Price 80s.

It was to the courageous enterprise of the House of Longmans that we owed the publication in English of the first "Comprehensive Treatise on Inorganic and Theoretical Chemistry" by J. W. Mellor, perhaps the only person in Great Britain endowed with the qualities necessary for the successful composition of such a work. Now we can welcome, again owing to the enterprise of the same publishing firm, the first of three or four volumes of a comprehensive treatise on Physical Chemistry, and again we can recognise in the author perhaps the only one in Great Britain who has the knowledge, teaching experience, literary ability and physical energy required for the task. Congratulations may be offered to both publisher and author. Since an undue extension of the period of publication is one of the dangers to which all comprehensive treatises must be subject, it is gratifying to learn that the second volume of this work is already in the press.

The author adopts the van't Hoff definition of physical chemistry as "the science devoted to the introduction of physical knowledge into chemistry, with the aim of being useful to the latter," and the present work is intended to present this field of science as a whole. The term "advanced" occurring in the title refers to the size and scope of the work rather than to its difficulty. Its principal aim is to give information to those in search of it and not to train students or even to "make readers think"; and the author believes in encouraging an open and receptive attitude towards original thought rather than in producing an attitude of scepticism and unreceptiveness. While dealing fully with the relevant theory, due regard will be given to descriptions of experimental

methods; and it is intended to assemble "empirical or semi-empirical formulae which are likely to be of interest to laboratory workers or to chemists or engineers engaged in large-scale work, who often require quantitative data not available which can be calculated with sufficient approximation for their needs by means of such formulae."

In view of the author's well-known interest in the history of science, it is not surprising to learn that the treatment of a section often begins with a short historical survey. Such a survey, even if it may not be, as the author thinks, to the taste of all readers, is essential in a comprehensive treatise and will, the reviewer believes, be welcomed by most readers.

Practically half of the present volume is taken up with a mathematical introduction, dealing with the elements of the calculus and passing on to differential equations and Fourier's series, and with an account of the principles of thermodynamics, the kinetic theory of gases, statistical mechanics and wave mechanics. There then follow sections on thermometry, high and low temperatures, and a long section on the properties of gases.

Whether in a treatise such as that under review, which will presumably be used not by the undergraduate but by the graduate student and specialist worker in physical chemistry, the space of 114 pages should be allotted to a mathematical introduction is no doubt a matter of opinion; but the thought occurs that either the reader will have already passed beyond the need for such a condensed treatment of mathematics, or such a condensed treatment will fail to meet his needs. The author, however, is a teacher of long experience and respect must be paid to his judgment. In any case, one can recognise the excellence of the author's treatment of the subject. A special word of praise must be given to the clearness of the type in which the mathematical formulae are printed. Even the smallest symbols are readily legible without eye-strain.

Of the work as a whole, one can speak only in terms of the highest praise. The book is eminently readable and the author writes with the knowledge and lucidity of style with which his previous works have made us familiar. No doubt a few minor errors or misprints occur—a few such have been noticed—but it is obvious that the author has taken great pains to secure the maximum degree of accuracy. Although one hesitates to question the author's accuracy in matters of historical detail, one statement has caught the reviewer's eye which seems to call for comment. On p. 510 the author states that "the first to obtain liquid hydrogen in bulk was Dewar in 1895." Is this really correct? In 1895, Dewar, by the expansion of hydrogen at -200° obtained a jet of gas along with a liquid; but he himself describes the production and *collection* of liquid hydrogen as being carried out for the first time on May 10th, 1898.

All students and workers in the field of physical chemistry, and all teachers of physical chemistry, will be grateful to Professor Partington for his *Advanced Treatise*, and one can only express the hope that the author will be able to bring this truly monumental work to a conclusion at not too distant a date.

ALEX. FINDLAY

OUTLINES OF PHYSICAL CHEMISTRY. By F. DANIELS, Ph.D., B.Sc. Pp. viii + 713. New York: John Wiley & Sons Inc. London: Chapman & Hall, Ltd. 1948. Price \$5.00; 40s.

Appearing first in 1913, Dr. F. H. Getman's "Outlines of Physical Chemistry" has passed through seven editions, the last four of which have been Dr. Daniels' complete responsibility. His revisions have been so extensive that nothing remains of Dr. Getman's original work, so the present edition has been issued under Dr. Daniels' name as the first edition of a new book. However, it is still recognisable to the reviewer who learned his physical chemistry with the aid of the last edition of "Getman and Daniels." Much has been revised and recent work has been added, including data (*e.g.*, on p. 646) from journals published in 1948, the year of publication of the book, a creditable achievement in a textbook for degree students. A table of stable and unstable isotopes (pp. 647-654) gives data on all 96 elements to curium, including the artificial products of the atomic pile.

Turning the pages, the reviewer noticed the heading "Transmutation" and was interested to learn (on p. 664) that the aim of the alchemist has been reversed. It is now profitable to transmute gold into mercury. A quantity of the stable mercury isotope ^{198}Hg has been prepared in an atomic pile from gold, which occurs naturally as the single isotope ^{197}Au ; this isotope of mercury gives a strong narrow spectral line at 5461 \AA ., which may well become the primary standard of length in preference to the cadmium red line, which is about double the width and requires a higher temperature of excitation. As natural mercury is a mixture of seven stable isotopes each giving its own spectral line of slightly different wavelength, it cannot be used for accurate measurement.

The scope of the book is wide, and covers all aspects of physical chemistry at degree level; there are many clear diagrams and a large selection of problems at the ends of the chapters. The text ranges from the correct pronunciation of "entropy" (p. 143) to an appendix which includes the mathematical development of the Debye - Hückel theory (p. 680).

In the usual three-letter abbreviation for "electro-magnetic units" (p. 396), the omission of both punctuation and spacing produces a slightly zoological effect.

J. B. ATTRILL

THE ANALYTICAL CHEMISTRY OF INDUSTRIAL POISONS, HAZARDS AND SOLVENTS. By M. B. JACOBS, Ph.D. Second Edition. Pp. xviii + 788. New York and London: Interscience Publishers Inc. 1949. Price \$12.

This book was first published in 1941 (Review, *Analyst*, 1941, 66, 477); it has now been considerably enlarged, and it aims to cover the field of analytical chemistry of industrial poisons exhaustively. In his first edition, Dr. Jacobs modestly hoped that his work would be useful in industry . . . and for chemists and toxicologists. He was certainly right. The book is most useful and indeed the reviewer knows of no other book covering this ground that is so comprehensive and contains so much information. To the analyst who has occasion to work in this field it is indispensable, not only describing all the appropriate methods of testing, but also giving information on the physiological effects, limits of tolerance and toxicity of a great range of products from the point of view of an industrial hazard.

The author has greatly extended the analytical parts of the work; he has called in aid all kinds of newer techniques, electrical and mechanical, as well as physico-chemical and chemical methods. The enumeration and study of dust particles is well described; so also are questions of fire and explosion risks as well as purely physiological effects. The range of compounds covered and the enumeration of specific sensitive reactions for so many of them is a most valuable feature; the author has evidently roamed very thoroughly over the literature to find and describe with an intimacy of detail so many specific and useful methods. Notable, also, is the inclusion of newer reactions—or should one say newer applications of old reactions—for the detection of traces of elements such as arsenic, lead, antimony, fluorine; and methods suitable for residues from fumigation and to compounds new to industry, such as tetramethylsuccinonitrile, which is used in the blowing of sponge rubber. Altogether the work contains a wealth of information which is of great value to the practising chemist in very many fields.

H. E. COX

MODERN SYNTHETIC RUBBERS. By HARRY BARRON. Third Edition. Pp. xix + 636. London: Chapman & Hall Ltd. 1949. Price 45s.

The two previous editions of this book have been reviewed in *The Analyst* (1943, 68, 97; 1944, 69, 199). Their arrangement and style are closely followed by the third edition, but this is very considerably expanded by the inclusion of knowledge gained during the war and subsequently released in a large number of publications, notably by the Combined Services Intelligence Reports on German industry. The value of the book has been greatly enhanced by these additions but they are also, at least partly, responsible for an increase in price of 17s., which must deter many who would otherwise buy the new edition.

Methods of analysis of synthetic rubbers are discussed in the final chapter, which is now expanded from 17 to 29 pages. The extent of this increase is, however, somewhat illusory because the extra space is largely occupied by tabulated properties of various materials. There are only three additional references to the literature, and one of these—Ministry of Supply, Users' Memorandum No. U.9—is not discussed in the text. This pamphlet shows how to estimate natural rubber by oxidation to acetic acid, a reaction not undergone by GR-S, so that Barron's statement (p. 580) that "analysis will not show up any marked difference" is not justified—in fact, on pp. 591 and 593 he himself describes colour tests to distinguish between them!

G. H. WYATT

THE CIVIL SERVICE COMMISSIONERS invite applications for a permanent appointment as Senior Examiner (Male) in the Ministry of Fuel and Power. Candidates must be at least 30 years of age on 1st January, 1950. They must possess an honours degree in physics with chemistry as a subsidiary subject, or an honours degree in chemistry with physics as a subsidiary subject, and must have had at least five years' experience in industrial research. Inclusive salary scale £750-£1,000. Further particulars and application forms from the Secretary, Civil Service Commission, Scientific Branch, 7th Floor, Trinidad House, Old Burlington Street, London, W.1, quoting No. 3126. Completed application forms must be returned by 29th September, 1950.

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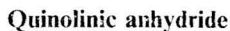
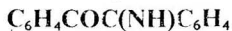
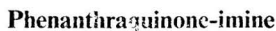
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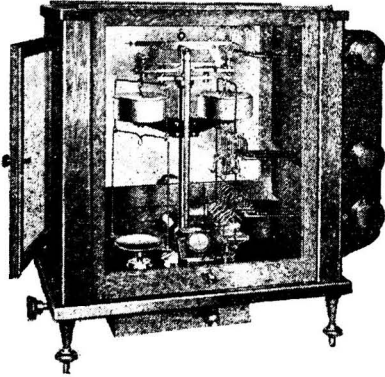
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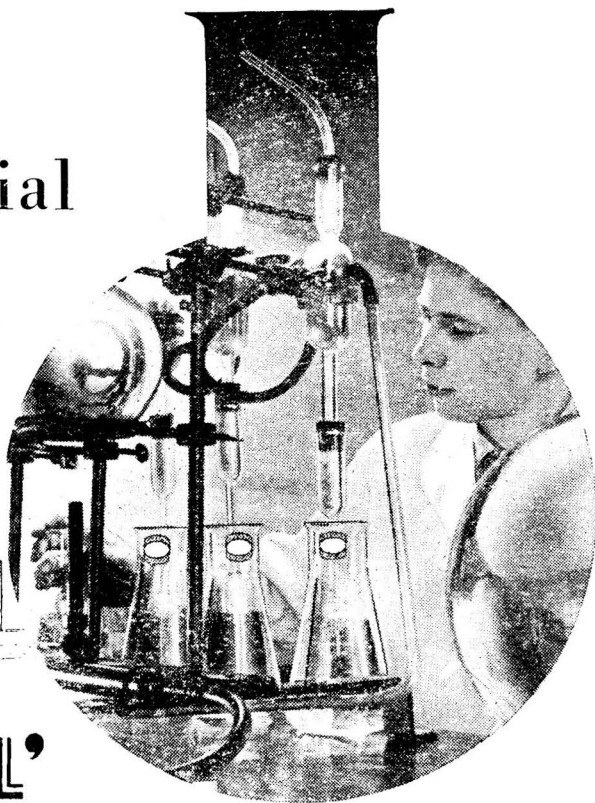
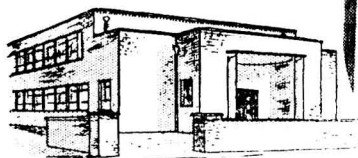
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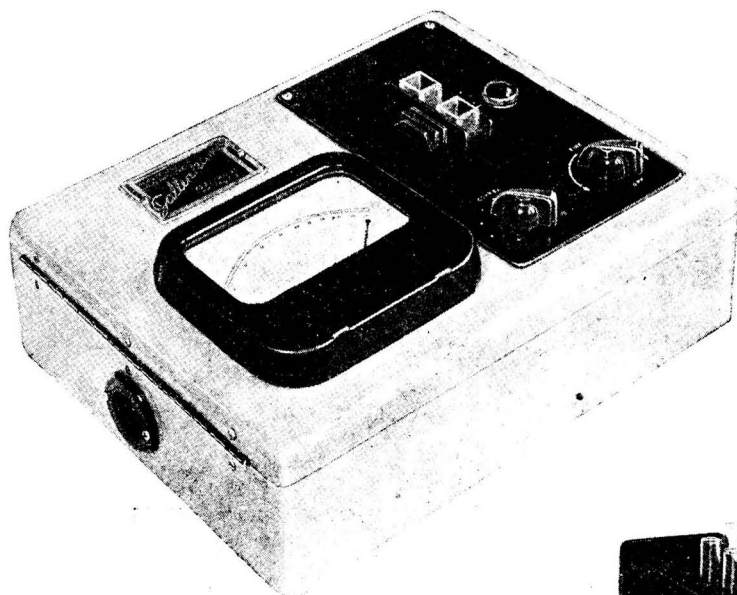
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