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dealing with all branches
of Analytical Chemistry:
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of Public Analysts and
Other Analytical Chemists



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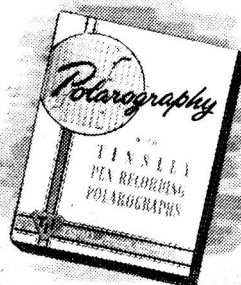


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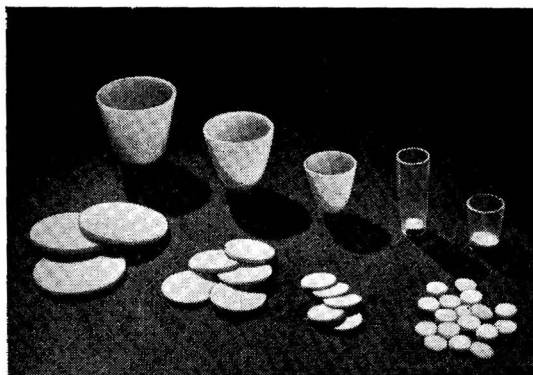
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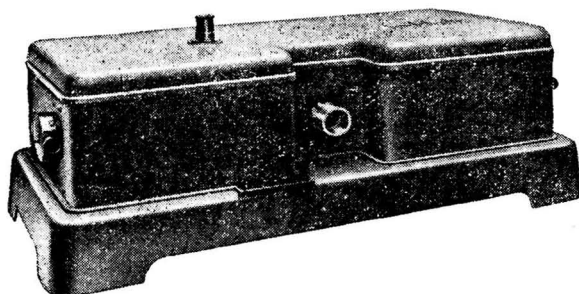
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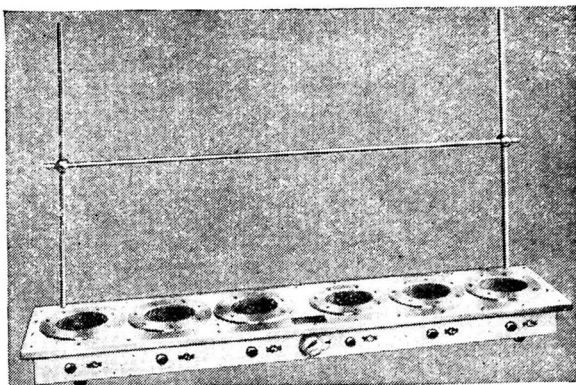
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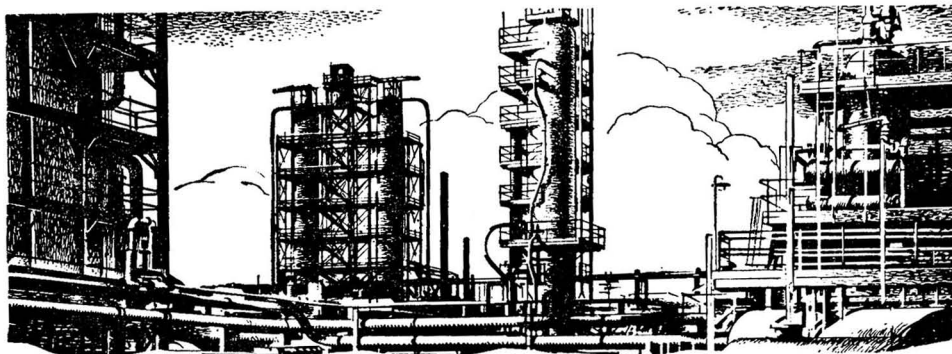
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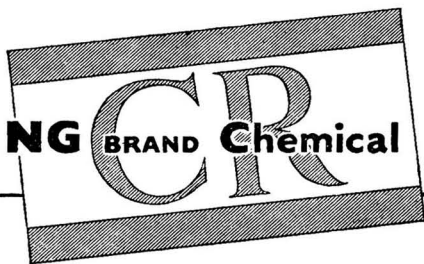
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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 7 p.m., on Wednesday, May 3rd, 1950, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The chair was taken by the President, Mr. George Taylor, O.B.E., F.R.I.C.

The following papers were presented and discussed: "The Testing of Atmospheric Conditions in Theatres and Cinemas," by J. F. Clark, M.Sc., A.R.C.S., D.I.C., F.R.I.C., F.A.C.I.; "Determination of Fluoride by Etching," by H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.; "Observations on the Spectrophotometric Estimation of Vitamin D," by H. E. Cox, Ph.D., D.Sc., F.R.I.C.; "The Analysis of Petrol - Kerosine Mixtures, with Special Reference to the Boiling-Point," by C. H. Manley, M.A., F.R.I.C.

NEW MEMBERS

John Barry Aldred, B.A. (Cantab.), A.R.I.C.; John Benson, A.R.T.C. (Salford); Edward James Boorman, A.R.C.S., B.Sc., D.I.C., Ph.D., F.Inst.P.; Leonard Tandy Bower, A.R.I.C.; Philip Hervey Daniels, F.R.I.C.; Frank Philip Gloyns, M.Sc., Ph.D., F.R.I.C., F.R.P.S.; Harry Munroe Napier Hetherington Irving, M.A., D.Phil. (Oxon.), F.R.I.C.; James Little, A.R.I.C.; Patrick Noel O'Donoghue, B.Sc. (Cork); James Ivor Phillips, A.R.I.C.; Arnold Singer; Ram Saran Srivastava, M.Sc. (India); Eric Hubert Steiner, B.Sc., F.R.I.C.; Joy Pamela Stern, B.Sc., Ph.D. (Lond.), A.R.C.S., D.I.C., A.R.I.C.; Sheila Donnelly Swift, B.Sc., M.Sc. (Cork); Donald Bryce Taylor, F.R.I.C.; Leonard George Tew; Russell Frederick Tomlinson, A.M.C.T., A.R.I.C.; Cyril Cecil Washbrook, A.R.I.C.; Charles Joseph Xuereb, M.D., B.Sc., Ph.C. (Malta).

DEATHS

WE regret to record the deaths of

Alfred Joseph Bull.
John Hanley.
Gavin Lawson.
Walter James Rees.
Harold George Tribley.

PHYSICAL METHODS GROUP

THE Twenty-fifth Ordinary Meeting of the Group was held at 5 p.m., on Friday, April 21st, 1950, in the Physical Chemistry Laboratory, Cambridge. The meeting, which had been preceded by a visit to the Cambridge Instrument Company's Works, was organised by the Polarographic Discussion Panel. Mr. B. S. Cooper, Chairman of the Group, opened the meeting and invited Mr. J. Haslam, Chairman of the Polarographic Discussion Panel, to occupy the chair for the rest of the meeting.

The following papers on Polarographic Analysis were read and discussed: "The Polarographic Determination of Aluminium," by G. Jessop, M.Sc., Ph.D.; "The Ilkovic Equation—its Present Status," by W. Cule-Davies, D.Sc., Ph.D., A.R.I.C.; "An Electronic Polarometer for Metallurgical Purposes," by C. H. R. Gentry, B.Sc., A.R.I.C.

The meeting concluded with a vote of thanks to the speakers and to the Cambridge Instrument Company for their hospitality.

REPRESENTATIVES OF THE SOCIETY ON COMMITTEES OF OTHER BODIES

THE following have been appointed by the Council to represent the Society on Committees of other bodies—

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Sampling of Oils and Fats	K. A. Williams
Chemical Symbols and Abbreviations	J. G. A. Griffiths
	E. C. Wood
Volumetric Mouldblown and Lampblown Glassware ..	W. F. Elvidge
	K. A. Williams

Glassware for Pharmaceutical Purposes	K. A. Williams
Standard Distillation Apparatus	D. D. Moir
Filtration Apparatus	Miss I. Hadfield
					G. H. Wyatt
Standardisation of the Orsat Apparatus	E. S. Hawkins
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Hydrogen Ion Concentration	J. E. Page
Boiler Water	R. Lessing
Chemical Analysis of Rubber	G. H. Wyatt
MINISTRY OF FOOD—					
Detection of Token Nutrients Added to Flour	D. W. Kent-Jones

The Analytical Chemistry of Bromine Manufacture

The following five papers were read at the Meeting of the Society on Wednesday, April 5th, 1950.

Part I. The Determination of Bromine in Brine

BY J. HASLAM AND G. MOSES

SYNOPSIS—The fluorescein, aeration and electrolytic methods of determination of bromine in brine are discussed and these methods compared with the hypochlorite oxidation test. In connection with the latter test, consideration has been given to the preparation of reagents, to the effect of calcium and magnesium on the test, as well as to the effect of variation of the pH of the solution to be oxidised. Observations are made on the efficiency of the hypochlorite oxidation method.

In our preliminary work on this subject, use was made of Seaber's method,¹ which was devised as a means of testing goods for sea-water damage. In this test, the sample under investigation is treated with a strong solution of chromic acid, and the liberated bromine is expelled from the solution by means of a stream of carbon dioxide. The gas evolved is then passed through a filter-paper impregnated with fluorescein. In this way a red eosin stain is produced on the paper and the intensity of the red colour varies with the amount of bromine in the sample. This test, although useful in our work in deciding the order of the bromine content of a sample, was not of the required degree of accuracy for quantitative work.

The next method investigated was devised as a result of an examination of the method put forward by B. S. Evans² for the determination of small amounts of bromides in chlorides. Similar aeration methods have been proposed by Baughmann and Skinner³ and by Francis and Harvey.⁴

The principle of the method devised by Evans² is the adjustment of the acidity of the chloride solution with sulphuric acid to between 8 and 9 *N*, followed by addition of chromic acid, which has a selective oxidising action on the bromide present in the sample. A stream of air is led through the oxidised solution for 1 hour and the liberated halogen is collected in a known volume of dilute sodium hydroxide solution. The sodium hydroxide solution is treated with a little sulphurous acid to reduce any hypobromite or hypochlorite to the corresponding halide, then neutralised with dilute sulphuric acid. The acidity of the solution

so obtained is adjusted to between 8 and 9 *N* with sulphuric acid, chromic acid added, and a stream of air is led through the apparatus; the liberated halogen is collected this time in standard arsenious oxide solution. After the air stream has been passed for 1 hour, the excess arsenious oxide is titrated with standard iodine solution, using starch solution as indicator.

Our investigations of this method indicated that the total halogen evolved in the oxidation increased with the time of aeration, and we came to the conclusion that the selection of an arbitrary aeration time of 1 hour could lead only by chance to the correct results for bromine. We did show, however, that chromic acid alone was a more selective oxidising agent than sulphuric - chromic acids and that, with chromic acid, the amount of halogen evolved after a certain time became constant. We developed a process along these lines, but the aeration times involved were long, *i.e.*, of the order of 7 hours in each aeration. When the method was applied to mixtures of 10 g. of sodium chloride and known amounts of pure potassium bromide, we obtained these results—

Bromine added, g.	Bromine found, g.
0.00427	0.00400
0.00427	0.00416
0.00160	0.00152
0.00160	0.00148

Subsequently, our attention was drawn to an electrolytic method of determination of bromine in brine, provided by I.C.I. (General Chemicals Ltd.). This method is based on the electrolytic oxidation of bromide to bromate in a hot solution of the salt made strongly alkaline with sodium hydroxide. A small amount of hypochlorite is usually formed, and this is reduced by formic acid in a buffered solution. The reduction of the hypochlorite by formic acid takes place readily in the hot solution, and it is unnecessary and inadvisable to boil the solution. After cooling, potassium iodide is added and the acidity adjusted. Interaction between the bromate and iodide liberates six equivalents of iodine and this is determined by titration with standard sodium thiosulphate solution.

METHOD

GENERAL REAGENTS—

Dilute hydrochloric acid (1 + 2)—An approximately 3.85 *N* solution.

Formic acid—A 90 per cent. solution.

Sodium hydroxide—A 5 *N* solution.

Sodium carbonate—Saturated solution.

Sodium acetate—A 20 per cent. w/v solution of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$.

Potassium iodide—A 10 per cent. w/v solution.

Starch solution—A 0.5 per cent. w/v solution.

STANDARD SOLUTIONS—

Sodium hydroxide—A *N* solution.

Sodium thiosulphate—A 0.1 *N* solution.

INDICATORS—

Methyl orange—A solution containing 2.0 g. per litre.

Methyl red—A solution containing 0.5 g. per litre.

PROCEDURE—

Measure 100 ml. of the sample of brine into a 150-ml. beaker and add 2 ml. of sodium carbonate solution and 2 ml. of 5 *N* sodium hydroxide solution. Heat to boiling, add a small amount of paper pulp, and allow the solution to stand until the precipitate settles. Filter the solution through a Whatman No. 40 filter-paper into a 250-ml. tall beaker; wash the precipitate with water containing 5 ml. of sodium carbonate (saturated, 2 *M*) and 5 ml. of 5 *N* sodium hydroxide per litre. To the filtrate add dilute hydrochloric acid solution until it is neutral to methyl orange, then make alkaline by addition of 0.5 ml. of *N* sodium hydroxide and bring to the boil. Oxidise by electrolysis, using a hollow cylinder of fine platinum gauze (5 cm. in height \times 4 cm. in diameter) reaching to the bottom of the beaker as anode and a stout platinum wire just dipping into the solution as cathode. Pass a current

of 0.4 amp. for 1 hour through the solution, which should be kept at a temperature of 90° to 100° C., with the beaker covered with a split watch glass to prevent evaporation. After oxidation of the bromide to bromate, rinse the glass cover and electrodes with hot water and treat the solution in the following manner.

Add 20 ml. of sodium acetate solution and 3 ml. of formic acid solution to the hot solution. Set aside for 2 to 3 minutes and then add 4 drops of methyl red indicator. If the colour is discharged within an interval of 5 minutes, warm the solution gently and, after cooling slightly, test again with a further 4 drops of indicator. Repeat this process until the colour persists. Boiling is unnecessary and is liable to decompose the bromate.

Cool the solution to room temperature, add 5 ml. of potassium iodide solution, dilute with water to approximately 200 ml. and add, while stirring, 16 ml. of dilute hydrochloric acid solution. Allow the solution to stand in the dark for 5 minutes, and then titrate immediately with 0.1 *N* sodium thiosulphate solution with starch solution as indicator.

1 ml. of 0.1 *N* sodium thiosulphate solution \equiv 0.00133 g. of bromine.

Carry out a "blank test" with a volume of distilled water equal to that of the electrolysed solution by adding the 20 ml. of sodium acetate solution and continuing as above from that point.

NOTES ON THE METHOD

The quantities of sodium acetate solution and dilute hydrochloric acid are for a final volume of solution of 200 ml. For larger volumes of solution, these reagents should be added in proportionally greater quantities.

After titration as above, the colour will return very slowly if the solution is allowed to stand, but not sufficiently to interfere with the correct end-point. Should the colour return rapidly and persistently it is an indication that the solution has been incorrectly acidified. Insufficient acid results in only partial reaction between the iodide and bromate, whilst an undue excess causes chlorate to be decomposed with consequent liberation of iodine. In either event a rapid return of the blue starch-iodide colour occurs.

In the above method any iodide present will be included with the bromide, and if present in appreciable quantities, it must be determined separately and deducted.

Applied to known mixtures of 30 g. of sodium chloride (A.R.) and various amounts of potassium bromide, the above electrolytic test gave the results shown in Table I. Although

TABLE I

RESULTS OF ELECTROLYTIC METHOD APPLIED TO 30 G. OF SODIUM CHLORIDE (A.R.) AND VARIOUS AMOUNTS OF POTASSIUM BROMIDE

Added 0.02 <i>N</i> potassium bromide solution, ml.	Final titration,* 0.1 <i>N</i> sodium thiosulphate solution, ml.	Recovery,* %
2	2.26	93.3
2	2.22	
4	4.46	93.0
4	4.51	
6	6.76	93.5
6	6.71	
8	8.65	90.9
8	8.81	
10	11.11	92.5
		Average 92.6

* After allowance for the result of the blank test.

the electrolytic method was an advance on the chemical method that we had used previously, both methods failed to give results of the high degree of accuracy which we required.

Kolthoff and Yutzy,⁵ however, in 1937, put forward a volumetric determination of bromide (after oxidation to bromate in the presence of much chloride). This method was based on

earlier work of D'Ans and Höfer⁶ and Van der Meulen,⁷ and Kolthoff and Yutzy gave the following experimental procedure.

To a suitable (25 ml. or less) volume of the neutral bromide solution, add 1 g. of sodium dihydrogen phosphate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 10 g. of sodium chloride and 5 ml. of *N* sodium hypochlorite solution, heat just to boiling and add 5 ml. of sodium formate solution ($\equiv 2.5$ g. of the solid). After cooling the solution, dilute to 150 ml. and add 1 g. of potassium iodide, 25 ml. of 6 *N* sulphuric acid solution and 1 drop of 0.5 *N* ammonium molybdate solution. Titrate immediately with standard sodium thiosulphate solution, adding starch solution just before the end-point is reached.

A blank should be run under identical conditions, substituting an equal volume of water for the bromide solution. The blank is subtracted from the volume of thiosulphate required in the test.

The addition of 10 g. of sodium chloride may be omitted in the test and in the blank when the sample contains less than 25 micromoles of bromide.

From the results given by Kolthoff and Yutzy, the method appeared to be very promising and a detailed investigation was made, the points dealt with being considered under the separate headings.

INVESTIGATION OF THE KOLTHOFF AND YUTZY METHOD

PREPARATION OF THE REAGENTS—

Sodium hypochlorite reagent—The sodium hypochlorite reagent used by Kolthoff and Yutzy was prepared according to Van der Meulen (*loc. cit.*) by dissolving 71 g. of chlorine in 1500 ml. of water containing 88 g. of sodium hydroxide. This was diluted to 2 litres to give a solution normal in hypochlorite and 0.1 normal in hydroxide.

This rather troublesome method of preparation was avoided in this investigation by obtaining 14 to 15 per cent. sodium hypochlorite liquor (bromine-free) from I.C.I. (General Chemicals) Ltd., and carrying out determinations of hypochlorite and hydroxide previous to dilution and addition of sodium hydroxide solution to yield a reagent normal in hypochlorite and 0.1 *N* in hydroxide.

The hypochlorite strength is determined as follows—

Dilute 10 ml. of the strong hypochlorite liquor to 250 ml. with distilled water. Measure 25 ml. of the diluted sample into a beaker containing 0.5 g. of sodium bicarbonate. Titrate the solution with 0.1 *N* sodium arsenite until a drop of the liquid gives no iodine coloration when allowed to fall on a drop of 5 per cent. potassium iodide solution on a white tile. Now add 1 ml. of potassium iodide solution and continue the titration until the iodine colour disappears.

The approximate amount of sodium arsenite solution required is now known, and the test is repeated in the following way—

Run into a small beaker an amount of 0.1 *N* sodium arsenite less by 0.1 ml. than the amount found in the preliminary test. Add 25 ml. of the diluted sample together with 0.5 g. of sodium bicarbonate and 1 ml. of potassium iodide solution, and titrate with the sodium arsenite solution until the liberated iodine disappears. The normality of the strong hypochlorite liquor is calculated from this titration.

The proportion of hydroxide is obtained by taking 10 ml. of the original strong hypochlorite liquor, adding 30 ml. of neutral hydrogen peroxide solution (20 vol. and neutral to phenolphthalein) together with 5 ml. of neutral barium chloride (0.5 *M*). Add 1 ml. of phenolphthalein solution and titrate the hydroxide with 0.1 *N* hydrochloric acid, running the acid in slowly, with continual stirring, until the colour disappears.

Blank experiments on 10 ml. of the hypochlorite reagent and 2 g. of sodium acid phosphate gave final titrations against 0.1 *N* sodium thiosulphate of 0.03 to 0.04 ml.; this figure compares very favourably with that of 0.8 ml. of 0.01 *N* thiosulphate obtained by Kolthoff and Yutzy, presumably using 5 ml. of the hypochlorite reagent and 1 g. of sodium acid phosphate.

Sodium formate solution—Dissolve 30 g. of sodium hydroxide (pellets from sodium) in water and add carefully 32 ml. of 90 per cent. formic acid solution (A.R.) and dilute the solution to 100 ml. with distilled water.

Sodium acid phosphate—Solid dihydrate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$.

Potassium iodide (A.R.)—Solid.

Sulphuric acid solution—A 6 *N* solution.

Ammonium molybdate solution—Dissolve 2.9 g. of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in distilled water and dilute the solution to 100 ml.

Sodium thiosulphate solution—A 0.1 *N* solution.

Starch solution—A 0.5 per cent. w/v solution.

METHOD—

First neutralise 50 ml. of the solution to methyl red with either 0.1 *N* or 1 *N* sulphuric acid. Add 2 g. of sodium di-hydrogen phosphate, $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, followed by 10 ml. of the hypochlorite reagent, and bring the solution just to the boil. Then place the beaker containing the solution on the laboratory bench and add 10 ml. of sodium formate reagent.

Wash down the sides of the beaker and the cover glass with water and allow the solution to stand for 5 minutes; then transfer the beaker to a bath containing running water to complete the cooling process. When cool, add 240 ml. of water, followed by 2.0 g. of potassium iodide, 50 ml. of 6 *N* sulphuric acid and 1 drop of the ammonium molybdate solution. Titrate the liberated iodine with 0.1 *N* sodium thiosulphate solution using starch mucilage as indicator.

APPLICATION OF THE METHOD TO THE DETERMINATION OF BROMIDE IN MIXTURES OF SODIUM CHLORIDE - POTASSIUM BROMIDE

Pure potassium bromide was prepared by ignition of thrice re-crystallised potassium bromate (AnalaR) and the method of bromine determination given above was then applied to known mixtures of the bromide and 15 g. of sodium chloride, each contained in a total volume of 50 ml. The amounts of bromine taken were those that would make the ratio of bromide to sodium chloride comparable with that found in borehole brines.

The results obtained are given in Table II. The average recovery is 99.5 per cent., and the method is therefore much more efficient than the electrolytic method, where the average recovery is 92.6 per cent.

TABLE II

RESULTS OF KOLTHOFF AND YUTZY METHOD APPLIED TO 15 G. OF SODIUM CHLORIDE (A.R.) AND VARIOUS AMOUNTS OF POTASSIUM BROMIDE

Added 0.02 <i>N</i> potassium bromide solution, ml.	Final titration,* 0.1 <i>N</i> sodium thiosulphate solution, ml.	Blank (15 g. of sodium chloride and other reagents)		Recovery,* %
		0.18 } ml. of 0.1 <i>N</i> sodium 0.19 } thiosulphate solution		
2	2.40			101
2	2.45			
4	4.79			99.0
4	4.72			
6	7.17			99.6
6	7.18			
8	9.47			98.85
8	9.52			
10	11.88			99.0
10	11.89			
			Average	99.5

* After allowance for the result of the blank test.

COMPARISON OF THE KOLTHOFF AND YUTZY METHOD WITH THE ELECTROLYTIC METHOD

At the time of this investigation a survey was being made of the bromine content of brines from the Cheshire brinefield, and accordingly several brines were available for examination by both methods. The results obtained are given in Table III. On average, the figures obtained by the electrolytic method are 92.7 per cent. of the corresponding figures obtained by the Kolthoff and Yutzy method. This conclusion supports the evidence obtained about the relative efficiencies of the two processes in connection with the examination of sodium chloride - potassium bromide mixtures.

THE EFFECT OF THE PRESENCE OF CALCIUM AND MAGNESIUM SALTS ON THE
KOLTHOFF AND YUTZY TEST

As borehole brines contain appreciable proportions of calcium and magnesium salts, which are likely to be precipitated to a certain extent by solutions of sodium acid phosphate and hence to influence the pH at which the oxidation of bromide to bromate is carried out in Kolthoff and Yutzy's method, it seemed desirable to carry out experiments on the oxidation of bromide to bromate (*a*) on solutions of sodium chloride (AnalaR) of comparable chloride

TABLE III

COMPARISON OF KOLTHOFF AND YUTZY METHOD WITH THE ELECTROLYTIC METHOD

Bromine, g. per cubic metre of brine	
Kolthoff and Yutzy method	Electrolytic method
127.7	119.9
121.3	112.6
130.3	118.6
114.5	105.9
109.9	100.9
103.1	94.9
132.7	124.9
118.7	110.6
126.5	117.4
113.2	105.6
101.0	94.6
102.0	93.9
108.9	101.8
110.1	102.8
97.5	90.6
106.3	100.6
38.5	32.6
75.9	69.9
97.9	90.7
88.3	80.4
138.8	131.0
112.4	107.2
96.8	88.6
101.0	91.2
115.9	104.6

concentration to that of brines, and containing known amounts of pure potassium bromide, (*b*) on similar solutions which contained, in addition, amounts of calcium and magnesium corresponding to those present in average borehole brines, and (*c*) on similar solutions to those described under (*a*) but containing, in addition, amounts of calcium and magnesium salts much greater than those present in average borehole brines.

The calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, AnalaR) used was first examined for the presence of bromide. Forty grams of the salt were dissolved in water and the solution was diluted to 250 ml. Twenty-five millilitres of this solution were transferred to a beaker by means of a pipette and 25 ml. of sodium carbonate solution (20 g. of sodium carbonate, AnalaR, in 250 ml. of water) were added. The suspension was diluted to about 100 ml., then brought to the boil, and finally allowed to settle over-night.

The mixture was then filtered through a Whatman No. 40 filter-paper, the precipitate being washed three times by decantation and twice on the filter-paper. The clear filtrate was boiled down to 50 ml., 13 g. of sodium chloride (AnalaR) was added, and the solution was neutralised to methyl red with hydrochloric acid solution (10 ml. of hydrochloric acid (AnalaR) and 90 ml. of water), 0.6 ml. being required. The oxidation procedure of Kolthoff and Yutzy (p. 347) was then applied, a blank test being carried out on 13 g. of sodium chloride (AnalaR). The results obtained were as follows—

Experimental condition	Titration, 0.1 N sodium thiosulphate, ml.
4.0 g. of calcium chloride present	0.14 0.12
Blank test (no calcium chloride)	0.11 0.10

Evidently, therefore, the calcium chloride contained a negligible proportion of bromine.

Magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, AnalaR) was shown to contain a negligible proportion of bromine by a similar method.

The effect of calcium and magnesium salts on Kolthoff and Yutzy's method was now investigated. Solutions containing 15 g. of sodium chloride, 4 ml. of 0.02 *N* potassium bromide solution, and various amounts of calcium chloride and magnesium sulphate, all in a total volume of 50 ml., were examined by the Kolthoff and Yutzy oxidation. The results obtained are given in Table IV.

TABLE IV

EFFECT OF CALCIUM AND MAGNESIUM SALTS ON KOLTHOFF AND YUTZY METHOD

Added	Final titration, 0.1 <i>N</i> sodium thiosulphate, ml.
(a) 4 ml. of 0.02 <i>N</i> potassium bromide	4.89
	4.93
(b) 4 ml. of 0.02 <i>N</i> potassium bromide	} 4.92
0.123 g. of calcium oxide	
0.05 g. of magnesium oxide	4.92
(c) 4 ml. of 0.02 <i>N</i> potassium bromide	} 4.89
0.246 g. of calcium oxide	
0.10 g. of magnesium oxide	4.91
(d) 4 ml. of 0.02 <i>N</i> potassium bromide	} 4.25
0.492 g. of calcium oxide	
0.20 g. of magnesium oxide	4.50

Only in solution (*d*), where the proportions of calcium and magnesium salts added were approximately four times the corresponding amount present in an average sample of brine, was a low result obtained, and our own opinion is that this effect was probably due to the mechanical difficulties involved in carrying out an oxidation of bromide to bromate in the presence of a very heavy precipitate of calcium and magnesium phosphates.

THE EFFECT OF VARIATION OF THE pH OF THE SOLUTION TO BE OXIDISED ON
THE RESULTS OBTAINED IN THE TEST

Although comparatively large amounts of calcium and magnesium did not affect the efficiency of the bromide oxidation, it was felt that their precipitation by sodium acid phosphate in the course of the test was likely to influence the pH at which the oxidation was conducted. Accordingly it was decided to carry out experiments to investigate the matter.

Solutions were prepared containing 15 g. of sodium chloride and various proportions of calcium as calcium chloride and magnesium as magnesium sulphate, in a total volume of 50 ml., and to these solutions were added 2 g. of sodium acid phosphate and 10 ml. of the sodium hypochlorite reagent. The pH of the suspensions was determined by means of the glass electrode, with the following results—

	Added, g.	pH of suspension
Calcium oxide	nil	5.40
Magnesium oxide	nil	5.40
Calcium oxide	0.123	5.02
Magnesium oxide	0.05	5.06
Calcium oxide	0.492	4.49
Magnesium oxide	0.20	4.52

Fifty millilitres of an average sample of a borehole brine, after neutralisation to methyl red with 0.1 *N* hydrochloric acid, gave, on similar treatment to the above, suspensions of pH (*a*) 4.96 and (*b*) 5.00. Solutions were then prepared containing 15 g. of sodium chloride (AnalaR), 4 ml. of 0.02 *N* potassium bromide solution, and varying amounts of either *N* hydrochloric acid (AnalaR) solution or *N* sodium hydroxide solution in a total volume of 50 ml. To such solutions were then added 2 g. of sodium acid phosphate and 10 ml. of hypochlorite reagent, the pH of the resulting solutions being then determined by means of the glass electrode. Corresponding solutions were also prepared and oxidised as usual by the method of Kolthoff and Yutzy with the results shown in Table V.

TABLE V

EFFECT OF pH OF SOLUTIONS PREPARED BY THE KOLTHOFF AND YUTZY METHOD

Added <i>N</i> hydrochloric acid solution, ml.	pH of solution prior to oxidation of bromide	Colour of solution in course of oxidation	Final titration, 0.1 <i>N</i> sodium thiosulphate, ml.
8.0	3.54	Distinctly yellow	2.77
8.0	3.52	"	2.84
6.0	4.12	Yellow	4.89
6.0	4.12	"	4.88
4.0	4.58	Pale yellow	4.90
4.0	4.58	"	4.91
2.0	4.90	Colourless	4.92
2.0	4.90	"	4.90
nil	5.35	Colourless	4.92
nil	5.35	"	4.89
Added <i>N</i> sodium hydroxide solution, ml.			
10	7.34		4.93
10	7.37		4.91
13	8.96		4.36
13	8.97		4.81
16	9.63		2.17
16	9.63		0.98
20	10.02		0.35
20	10.02		0.45

The results obtained show that the oxidation of the bromide to bromate was quantitative over the pH range 4.12 to 7.35. There is little doubt that, in the application of Kolthoff and Yutzy's method to normal samples of brine, the pH of the solution prior to oxidation lies well within this pH range.

THE BEHAVIOUR OF IODIDES IN THE OXIDATION TEST

Although the brines normally met with in the course of our work contained negligible proportions of iodine (as shown by the method of Andrews and Mandeno⁸) it was thought that the influence of iodides on the Kolthoff and Yutzy test should be known. Accordingly, solutions were prepared which contained known amounts of pure potassium iodide and 15 g. of sodium chloride in a total volume of 50 ml. These solutions were then oxidised by Kolthoff and Yutzy's procedure with the results given in Table VI.

TABLE VI

EFFECT OF IODIDES ON KOLTHOFF AND YUTZY METHOD

Added 0.02 <i>N</i> potassium iodide solution, ml.	Final titration,* 0.1 <i>N</i> sodium thiosulphate solution, ml.	Recovery,* %
2	2.35	98.4
2	2.37	
5	5.88	98.2
5	5.90	
10	11.86	98.7
10	11.83	

* After allowance for the result of the blank test.

Evidently iodide is oxidised to iodate in the oxidation test, and hence it should be borne in mind that figures for the bromine content of brines determined by this method are inclusive of any iodine present in the samples unless this element has been determined separately and the amount present deducted.

THE DETERMINATION OF VERY SMALL AMOUNTS OF BROMIDE

It was necessary to consider whether the method of Kolthoff and Yutzy was applicable to the determination of very small amounts of bromide in water. Known amounts of pure potassium bromide in a volume of 50 ml. of solution were oxidised by Kolthoff and Yutzy's procedure with the following satisfactory results—

Bromine added, g.	Bromine found, g.
0.00008	0.00007
	0.00007
0.00016	0.00015
	0.00015

The work described in the remainder of this paper was carried out in collaboration with D. N. Fogg.

A determination was made of the upper limit of the amount of potassium bromide which is quantitatively oxidised to bromate by means of 10 ml. of *N* hypochlorite solution, using our normal procedure (p. 347). Known amounts of pure potassium bromide, prepared by heating thrice-recrystallised potassium bromate, were subjected to the hypochlorite oxidation procedure (*a*) when dissolved initially in 50 ml. of water, and (*b*) when dissolved initially in 50 ml. of water containing 15 g. of sodium chloride (A.R.). The results obtained are given in Table VII. With the aqueous solution the oxidation proceeds satisfactorily up to 0.0317 g. of potassium bromide and with the sodium chloride solution up to 0.0793 g. of potassium bromide.

TABLE VII

Potassium bromide added, g.	Calculated titration after complete oxidation of bromide to bromate, 0.1 <i>N</i> sodium thiosulphate, ml.	Experimental titration*	
		(<i>a</i>) in absence of sodium chloride, 0.1 <i>N</i> sodium thiosulphate, ml.	(<i>b</i>) in presence of 15 g. of sodium chloride, 0.1 <i>N</i> thiosulphate, ml.
0.0099	5.0	4.98 4.98	4.96 4.96
0.0159	8.0	7.94 7.95	7.93 7.94
0.0198	10.0	9.91 9.92	9.88 9.89
0.0238	12.0	11.90 11.89	11.87 11.89
0.0278	14.0	13.87 13.87	13.92 13.93
0.0317	16.0	15.79 15.77	15.86 15.86
0.0357	18.0	17.55, 17.21, 17.83, 17.56	17.84 17.84
0.0397	20.0	17.85, 17.83, 19.52, 19.25	19.84 19.81
0.0496	25.0	20.25 21.16	24.81 24.77
0.0595	30.0	23.14 22.10	29.84 29.84
0.0793	40.0	25.0 25.0	39.76 39.74
0.1190	60.0	32.15	57.50
0.1488	75.0	38.70	55.15
0.1884	95.0	43.0	55.15

* After correction for result of blank.

Results of blank determinations—

	0.1 <i>N</i> sodium thiosulphate, ml.
(<i>a</i>) In absence of sodium chloride	0.02 0.03
(<i>b</i>) In presence of 15 g. of sodium chloride, A.R.	0.16 0.16

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Part II. The Bromine Content of the Cheshire Salt Deposit and of Some Borehole and other Brines

BY J. HASLAM, E. C. ALLBERRY AND G. MOSES

SYNOPSIS—The paper reports an analysis of the core of a single borehole through the Cheshire salt deposit. The results of complete analyses of the water-soluble and insoluble portions of an average sample of the core are given, together with figures which show the variation in bromine, sodium chloride and water-insoluble matter with depth. It is shown that, although the concentrations of the salt and insoluble matter vary considerably, the bromine distribution is sensibly constant. The bromine and chloride concentration in various brines and their variation with time are included. A description is given of the sampling procedure and analytical methods used, and in particular of the application of the analytical procedures for bromine described in the preceding paper.

METHODS for the determination of bromine in various brines having been established, it was subsequently decided to carry out an investigation of the Cheshire salt deposit. Although much was known about the impurities in brine prepared from this deposit, little was known about the proportion of bromine present in various parts of the borehole.

A core from a borehole was preserved for this investigation. The pieces of core were brought from the borehole to a shed where they were laid on the ground and numbered by the borer, who marked fiducial points corresponding to his measured depths, which were about 10 metres apart. As it had been decided to sample the core in equal lengths, these were marked off, the depth of each length below rockhead being referred to the measured depths.

In turn, each cylindrical piece forming part of the length was placed on a table, and filed and brushed to remove loose and projecting pieces of salt and marl; this debris was rejected. The piece was then filed uniformly along a generator. This gave a pile of powder which was collected; on the assumption that the core was homogeneous in a direction perpendicular to its length (as it usually appeared to be) it was a fair sample of the piece.

When a sample had been so removed from each piece in a length, portions of the samples were mixed in amounts judged to be proportional to the sizes of the pieces. The resulting mixture, about 200 g. of substance, was taken as being a fair sample. A few pieces had broken into small lumps before they reached the storage shed; these and such pieces as were obviously not horizontally homogeneous were filed so as to give what was judged to be a fair sample. The filing was done with a Firth Brown Millenicut file, which removed the required amount, about 50 g., from a piece in a few minutes: only six files were required for the whole core.

In all, 50 samples were available for examination. As a preliminary step, 2 g. were taken from each of the 50 samples, and the total of 100 g. was mixed thoroughly in order to prepare a fairly accurate sample of the complete core. Twenty grams of the average sample of the core were boiled with water, the mixture was filtered and the insoluble matter washed well with hot water until the washings gave no evidence of the presence of chloride. The insoluble matter was dried at 100° C., and the filtrate, which contained the soluble matter, was diluted to a weight of approximately 1000 g. Known weights of this dilute filtrate

were taken in the subsequent determination of soluble sodium, etc. The following analytical results were obtained—

Loss on heating sample to 100° C. = 0.6 per cent.

INSOLUBLE MATTER (after drying at 100° C.) = 24.7 per cent.—

	%
Loss on ignition	3.14
Silica (SiO ₂)	12.02
Ferric oxide (Fe ₂ O ₃)	1.29
Titanium dioxide (TiO ₂)	0.12
Alumina (Al ₂ O ₃)	3.28
Manganous oxide (MnO)	0.0054
Calcium oxide (CaO)	1.38
Magnesium oxide (MgO)	1.93
Sodium oxide (Na ₂ O)	0.09
Potassium oxide (K ₂ O)	0.87
Phosphoric anhydride (P ₂ O ₅)	0.044
Carbon dioxide (CO ₂)	1.86
Sulphuric anhydride (SO ₃)	0.37

SOLUBLE MATTER—

	%
Silica (SiO ₂)	0.02
Ferric oxide + aluminium oxide (Fe ₂ O ₃ + Al ₂ O ₃)	N.D.
Calcium oxide (CaO)	2.09
Magnesium (Mg)	0.04
Sodium (Na)	27.3
Potassium (K)	0.07
Chlorine (Cl)	42.2
Sulphuric anhydride (SO ₃)	2.92
Bromine (Br)	0.0223

The above analytical figures have been recalculated as follows—

INSOLUBLE MATTER—

	%
Marly matter	20.26
Dolomitic limestone	3.82
Calcium sulphate	0.62

SOLUBLE MATTER—

	%
Sodium chloride (NaCl)	69.26
Calcium sulphate (CaSO ₄)	4.96
Potassium chloride (KCl)	0.133
Magnesium chloride (MgCl ₂)	0.116
Calcium chloride (CaCl ₂)	0.089
Sodium bromide (NaBr)	0.029

There is no evidence that the average sample contains other metallic elements, as is shown by the following report on the spectrographic examination, which was carried out by L. H. Cross—

“Sodium, silicon, iron and calcium are present in significant amounts. Small amounts of magnesium and aluminium and a trace of potassium are present.”

The 50 samples from the borehole were then examined individually, three determinations being carried out on each sample, *viz.*, (1) insoluble matter, (2) chloride content calculated as sodium chloride, and (3) bromine content.

In the determination of the insoluble matter, about 10 g. of the well-mixed sample were heated with 100 ml. of distilled water. After boiling, the mixture was allowed to cool. The insoluble matter was filtered off on a tared Whatman No. 40 filter-paper and washed four times with distilled water. The filter-paper and contents were placed in a weighing bottle and heated to constant weight in the oven at 100° C. The result was expressed as percentage of insoluble matter.

The filtrate from the determination of the insoluble matter was diluted to 500 ml. and a Volhard determination was carried out on 20 ml. of the dilute solution. The result was calculated as percentage of sodium chloride.

In the bromine determination, 10 g. of the well-mixed sample were weighed out into a 250-ml. beaker and digested with 30 ml. of water; when the soluble salts had been dissolved, 10 ml. each of strong sodium carbonate (100 g. of Na₂CO₃, AnalaR, per litre of distilled water)

and strong sodium hydroxide solution (50 g. of NaOH (from sodium) per litre of distilled water) were added, and the whole brought to the boil. When the solution was cool and the insoluble material had settled, it was filtered through a Whatman No. 40 filter-paper and the insoluble matter was washed with about 100 ml. of dilute sodium carbonate - sodium

TABLE I

RESULTS OF EXAMINATION OF SAMPLES FROM CORE OF BOREHOLE

No. of sample	Composition of sample, g. per 100 g.			Ratio, g. of bromine to g. of chlorine
	Insoluble matter	Sodium chloride	Bromine	
TOP OF CORE				
1	8.7	88.0	0.0173	1 : 3086
2	8.0	89.9	0.0210	1 : 2597
3	10.6	84.9	0.0189	1 : 2725
4	32.4	58.7	0.0198	1 : 1798
5	45.8	48.4	0.0175	1 : 1678
6	11.5	84.8	0.0205	1 : 2509
7	12.1	84.0	0.0225	1 : 2265
8	12.6	82.9	0.0206	1 : 2441
9	5.4	89.1	0.0243	1 : 2224
10	8.0	86.0	0.0218	1 : 2393
11	5.1	88.8	0.0237	1 : 2273
12	20.3	72.9	0.0266	1 : 1663
13	43.4	49.2	0.0249	1 : 1509
14	49.0	42.0	0.0313	1 : 813.9
15	21.9	70.8	0.0242	1 : 1774
16	8.2	86.3	0.0210	1 : 2493
17	12.1	82.8	0.0222	1 : 2262
18	10.3	83.7	0.0210	1 : 2417
19	40.6	52.0	0.0284	1 : 1111
20	71.7	20.2	0.0254	1 : 480.6
21	13.6	81.2	0.0250	1 : 1980
22	9.5	86.2	0.0272	1 : 1923
23	3.4	94.5	0.0249	1 : 2302
24	12.4	81.1	0.0243	1 : 2024
25	35.8	56.1	0.0243	1 : 1401
26	46.5	44.9	0.0272	1 : 1012
27	20.3	74.6	0.0258	1 : 1754
28	18.7	74.8	0.0256	1 : 1772
29	25.1	66.1	0.0277	1 : 1447
30	15.7	77.4	0.0265	1 : 1772
31	21.2	73.4	0.0245	1 : 1818
32	16.5	78.1	0.0233	1 : 2033
33	4.2	92.3	0.0256	1 : 2187
34	10.5	84.3	0.0238	1 : 2141
35	17.6	76.5	0.0244	1 : 1092
36	10.2	85.0	0.0243	1 : 2121
37	72.8	18.8	0.0270	1 : 422.4
38	81.7	10.9	0.0258	1 : 256.3
39	17.5	77.1	0.0208	1 : 2249
40	9.6	86.9	0.0223	1 : 2358
41	9.0	88.6	0.0213	1 : 2523
42	11.3	84.7	0.0217	1 : 2368
43	11.6	83.6	0.0218	1 : 2326
44	6.6	90.4	0.0180	1 : 3047
45	47.7	46.2	0.0102	1 : 2748
46	60.1	33.3	0.0053	1 : 3811
47	38.0	57.9	0.0062	1 : 5665
48	47.8	45.3	0.0040	1 : 6879
49	73.2	19.1	0.0020	1 : 4602
50	85.8	6.8	0.0010	1 : 4125
BOTTOM OF CORE				

hydroxide solution (20 ml. of each of the above sodium carbonate and sodium hydroxide solutions in 1 litre of distilled water).

The filtrate was neutralised to methyl orange with dilute hydrochloric acid (prepared from AnalaR hydrochloric acid), and the neutral solution was boiled down to a volume of 50 ml., the bromine content being then determined by the method given in Part I (p. 347).

A blank experiment was carried out by taking 15 ml. each of the strong sodium carbonate solution and the strong sodium hydroxide solution, diluting to about 50 ml. with distilled water, neutralising with dilute hydrochloric acid using methyl orange as indicator, then boiling free of carbon dioxide and, after reduction of the volume to 50 ml. by further boiling, carrying out the oxidation as above. The result was calculated as percentage of bromine in the salt rock.

In the course of the above determinations, the sample was first boiled with a strong solution of sodium carbonate and sodium hydroxide, the insoluble matter filtered off, and the bromine determination carried out on the filtrate. It seemed desirable to prove that with our method of examination no bromine was left behind in this insoluble matter. Accordingly, the insoluble matter obtained from two bromine determinations carried out on one of the samples was collected together and washed into a 1-litre evolution flask (see Part I, ref. 2) with about 100 ml. of water. To this suspension was added 10 g. of chromic acid, and the flask was connected to a receiver containing 1 g. of sodium hydroxide in about 50 ml. of water. Fifty millilitres of concentrated sulphuric acid were then run in very slowly from the funnel, and the funnel was rinsed down with water. A guard tube containing 1 g. of sodium hydroxide in about 50 ml. of water was connected and air aspiration commenced. The mixture in the evolution flask reached a temperature of about 70° to 80° C. on the addition of sulphuric acid, and the marly material seemed to be completely disintegrated in the process.

A blank experiment was carried out at the same time using 100 ml. of water, 10 g. of chromic acid and 50 ml. of concentrated sulphuric acid. After aeration for 5 hours, the contents of the two receivers (experiment and blank) were each washed into 400-ml. beakers and 10 ml. of saturated sulphur dioxide solution added to each.

The following morning the solutions were neutralised to methyl red with dilute AnalaR hydrochloric acid (approximately 1 *N*) and the solutions were boiled free of sulphur dioxide, a small amount of dilute hydrochloric acid being added from time to time during the course of the boiling to preserve the acid reaction to methyl red. When free of sulphur dioxide and when the volume had been reduced to 50 ml., the solutions were cooled, neutralised to methyl red with *N* sodium hydroxide, and the bromine oxidation method was then applied. The following results were obtained—

	Final titration, ml. of 0.02 <i>N</i> sodium thiosulphate
Sample	0.10
Blank	0.10

From the above results we concluded that the bromine remaining in the insoluble portion of the salt rock when treated as described was negligible.

TABLE II

BROMINE AND CHLORINE IN REPRESENTATIVE BRINES

Chloride in brine, g. of NaCl per 100 ml.	Bromine in brine, g. per cubic metre	Ratio, g. of bromine to g. of chlorine
31.25	132.1	1 : 1435
30.95	130.0	1 : 1444
31.19	132.1	1 : 1432
30.77	128.5	1 : 1452
31.16	115.8	1 : 1632
31.25	110.6	1 : 1714
31.03	97.6	1 : 1929
30.75	150.0	1 : 1565
30.01	138.9	1 : 1310
30.84	120.3	1 : 1555
29.66	101.5	1 : 1773
30.22	106.2	1 : 1726
30.27	106.6	1 : 1722
29.72	110.7	1 : 1791
29.72	106.8	1 : 1689
31.36	124.9	1 : 1523
31.13	113.2	1 : 1668
31.30	97.9	1 : 1939
30.48	112.8	1 : 1640

The results obtained on examination of the various samples of salt rock are given in Table I. The interesting feature of these results is the comparatively small variation in the bromine content despite large changes in the chloride content caused by the presence of marl bands.

The brines normally used are obtained by artificial solution in water of the soluble constituents of the deposit. The bromine content of these brines varies considerably with the history of the borehole, but the ratio of bromine to chlorine is not constant, as will be seen from Table II, which gives the bromine and chloride content of a representative series of brines and the ratio of bromine to chlorine in these brines.

The variation with time which takes place in the bromine content of borehole brines is illustrated in the table below, in which the results of examination of typical brines from four individual boreholes are given at six-monthly intervals over a period of three years.

	6 months	12 months	18 months	2 years	2½ years	3 years
BRINE A						
Chloride content, g. of NaCl per 100 ml.	30.52	31.03	31.25	31.36	31.25	30.89
Bromine content, g. per cubic metre	116.1	113.9	108.7	109.0	110.6	107.5
Ratio Br : Cl	1 : 1594	1 : 1653	1 : 1744	1 : 1745	1 : 1714	1 : 1743
BRINE B						
Chloride content, g. of NaCl per 100 ml.	30.60	31.25	31.13	31.16	31.03	31.13
Bromine content, g. per cubic metre	113.4	121.3	102.3	95.1	97.6	91.5
Ratio Br : Cl	1 : 1637	1 : 1563	1 : 1846	1 : 1987	1 : 1929	1 : 2064
BRINE C						
Chloride content, g. of NaCl per 100 ml.	30.60	29.98	29.72	30.22	30.01	—
Bromine content, g. per cubic metre	116.6	109.8	119.3	134.9	138.9	—
Ratio Br : Cl	1 : 1592	1 : 1656	1 : 1511	1 : 1359	1 : 1310	—
BRINE D						
Chloride content, g. of NaCl per 100 ml.	31.46	31.46	31.33	31.49	31.36	31.03
Bromine content, g. per cubic metre	152.3	152.7	141.4	130.5	124.9	113.8
Ratio Br : Cl	1 : 1253	1 : 1249	1 : 1370	1 : 1480	1 : 1523	1 : 1654

The mixed brine obtained from this salt deposit varies to a certain extent in its bromine content as is shown by the following figures, which represent the bromine content of the brine at six-monthly intervals over a period of three years.

	6 months	12 months	18 months	2 years	2½ years	3 years
MIXED BRINE						
Chloride content, g. of NaCl per 100 ml.	30.52	30.54	30.63	30.63	30.54	30.69
Bromine content, g. per cubic metre	128.4	123.3	121.4	116.1	111.9	110.3
Ratio Br : Cl	1 : 1442	1 : 1503	1 : 1531	1 : 1601	1 : 1656	1 : 1689

Brines from the Middlewich (a so-called "wild" brine) and Preesall areas do not contain as high a proportion of bromine as the artificially prepared brines above, as is shown by the following figures—

	Middlewich brine	Preesall brine
Chloride content, g. of NaCl per 100 ml.	31.11	31.07
Bromine content, g. per cubic metre	101.8	80.46
Ratio Br : Cl	1 : 1855	1 : 2343

Part III. Survey of the In-Shore Waters Round the Coasts of Great Britain

BY J. HASLAM AND R. O. GIBSON

SYNOPSIS—The results are given of a survey of in-shore waters made in connection with the search for a suitable site for a plant for the extraction of bromine from sea-water. The methods used for the determination of the salinity, bromine content, chlorine demand, phosphate content, and alkalinity are described, together with methods used for the determination of salinity from rapid density observations.

IN 1938 serious consideration was given to the manufacture of bromine from sea-water. A great deal of information was obtained which ultimately led to the choice of a suitable site at Hayle, in Cornwall. In the course of this work it became obvious that although there was considerable knowledge of the salinity and temperature of the sea round the British Isles, the data on which this knowledge was based had been collected from stations at least 5 miles from the shore, and that there was little or no information available of the properties of in-shore waters. Consultation of the available records showed that the bromine content and excess base varied with the salinity within narrow limits for samples taken from off-shore stations, but that there was a possibility of local variations closer in-shore. It was learnt that little was known of the amount of organic matter present in either off-shore or in-shore water.

In view of the lack of information on in-shore water, it was decided to obtain and to examine samples of water from a number of in-shore stations round the coasts of Great Britain, so that this information could be used as the basis for a more detailed search for a suitable site for a bromine factory. In obtaining samples we were extremely fortunate in having the very considerable help of Mr. D. J. Matthews, formerly member of the Hydrographic Department of the Admiralty.

Sets of samples were collected by the Scottish Fishery Board's launch *Kathleen* off the coast from some miles south to some miles north of Aberdeen (Station 1), and by a local fisherman from Newburgh from a point off the mouth of the River Ythan, about 15 miles north of Aberdeen (Station 2). Dr. Tait (of the Scottish Fishery Board) also arranged for series of samples to be collected at three points off the north coast of the Moray Firth by the launch *Kathleen* (Stations 3, 4 and 5).

The officers of the Scottish Fishery Board on the west coast of Scotland kindly helped in arranging for samples to be collected by the lighthouse keeper at Rudh' Re (Station 6) and by a fisherman off the coast at Machrihanish on the Mull of Kintyre (Station 7).

Samples were also taken by the S.S. *Princess Maud* when outward bound for Stranraer with Corsewall Point abeam (Station 8); by L.M.S. mail steamer between Holyhead and Dublin with South Stack abeam (Station 9); by the lighthouse keeper from Bardsey Island (Station 10); and by the S.S. *St. David* from Fishguard with Strumble Head abeam (about 1 mile off-shore) (Station 11). In addition, Mr. Pender, the lifeboat coxswain at Sennen Cove, Cornwall, collected a series of samples from the lifeboat slipway (Station 12). Information was also obtained about the sea-water at other points, e.g., Cumberland, North Wales, Cornwall and Pembrokeshire.

Determinations of salinity and bromine were carried out on all the samples; soluble phosphate, chlorine demand and amount of acid required to bring the sea-water to an agreed pH were determined on some of the samples.

PRINCIPLES OF THE ANALYTICAL METHODS EMPLOYED

SALINITY—

A known volume of the sea-water was titrated with standard silver nitrate solution using potassium chromate as indicator. The silver solution was standardised by titration against sea-water of known chloride content obtained from Professor Knudsen, Polyteknisk Laereanstalt, Kobenhaven.

The chloride content of the sample under investigation was deduced from the results of this titration and reference to Knudsen's hydrographical tables; a further reference to these tables gave the salinity figure, which indicates the total weight of salts in grams per 1000 g. of sea-water.

BROMINE CONTENT—

One hundred millilitres of the sample of sea-water were first boiled down to 50 ml., and the solution was cooled and neutralised with 0.1 *N* hydrochloric acid using methyl red as indicator. The hypochlorite oxidation method was then applied (without further addition of sodium chloride), the final titration being carried out with 0.05 *N* sodium thiosulphate solution, using starch mucilage as indicator. After correction for the result of a blank experiment on the reagents, the bromine content of the sample was calculated in terms of g. per cubic metre.

CHLORINE DEMAND—

REAGENTS—Sodium hypochlorite solution—A solution was made of 2.55 ml. of *N* sodium hypochlorite solution (as used in the bromine determination) diluted to 1 litre with distilled water. This dilute solution contained 0.10 g. of available chlorine per litre.

***o*-Tolidine reagent solution—**This was a 0.1 per cent. w/w solution of *o*-tolidine in 10 per cent. v/v hydrochloric acid, as sold by the Candy Filter Co., Ltd., Hanwell, London.

METHOD OF TEST—Samples of 25 ml. of the sea-water to be tested were measured into separate clear colourless glass bottles (2-oz. narrow-necked). The dilute hypochlorite solution was now added in various amounts, *i.e.*, 0.2, 0.4, 0.6 ml., etc., the stoppers inserted, and the mixtures shaken thoroughly before allowing to stand on the laboratory bench for half an hour. One millilitre of the *o*-tolidine reagent was now added to each bottle, the contents were mixed and the solution allowed to stand for 5 minutes.

The colour which was equivalent to that obtained on the addition of 1 ml. of 0.1 per cent. v/v potassium chromate solution to 25 ml. of water was used as the basis of comparison, *e.g.*, if the colour obtained by the addition of 0.4 ml. of standard hypochlorite solution to 25 ml. of the sea-water under test followed by addition of *o*-tolidine was equivalent to the yellow chromate standard, then the chlorine demand of this sea-water was expressed as "less than 1.6 g. of available chlorine per cubic metre of sea-water."

PHOSPHATE DETERMINATION—

The method of determination of phosphate in samples of sea-water was that adopted by Dr. Cooper of the Marine Biological Research Station, Plymouth. This method was based on the reduction of phosphomolybdate by means of stannous chloride to yield blue-coloured complexes. It involved the evaluation of the reagent blank, and the use of this value in the determination of the apparent value of the sea-water under examination, as well as the evaluation of the apparent value of a sample of the sea-water enriched by a definite amount. The latter figures were then used to calculate the true phosphate figure of the sample, which was calculated in terms of mg.-atoms of phosphorus per cubic metre of sea-water.

Note—The "chlorine demand" and "soluble phosphate" contents were determined for a number of the samples first collected in an effort to obtain some idea of the amount of oxidisable matter present, which would increase the amount of chlorine required to displace the bromine in the manufacture of bromine from sea-water. The chlorine demand gave an indication of the amount of organic matter likely to be present later in the spring when this phosphate became used up by living organisms, *e.g.*, plankton. As it was found that the amount of chlorine which would have to be used to oxidise such organic matter would amount to 2 to 3 per cent. of that required to displace the bromine, it was decided that it was not worth studying the variation of this amount in detail and the determinations were discontinued.

AMOUNT OF ACID REQUIRED TO BRING THE SEA-WATER TO AN AGREED PH—

This was determined by titration of 100 ml. of the sea-water with 0.1 *N* sulphuric acid, using a glass electrode. Usually a pH of 3.5 was selected, and the amount of acid required to be added to the sea-water to reduce the pH to 3.5 was determined for a large number of

the samples and found to lie between 2.5 and 3.5 ml. of 0.1 *N* sulphuric acid per 100 ml. of the sea-water.

Calculated values of the "excess base" of those samples for which the acid required to bring the pH to 3.5 has been determined are given in the hope that these values, although not obtained by the standard method used in oceanography, may be of value to oceanographers.

The standard method is to add an excess of 0.05 *N* hydrochloric acid (carbon dioxide-free) to 200 ml. of sea-water, to boil free of carbon dioxide and to titrate back with carbon dioxide-free 0.05 *N* sodium hydroxide to a special mixed indicator which gives a colour change at pH 5.6. A number of sea-water samples were titrated electrometrically to pH 3.5 and then titrated back to pH 5.6, and it was found that the amount of sodium hydroxide required was fairly constant—an average figure for nine different samples of sea-water being 0.38 ml. of 0.1 *N* sodium hydroxide with high and low values of 0.42 and 0.30 respectively. This average value has therefore been subtracted from the amount of acid required to give a pH of 3.5 to give the "excess base" figure which is thought to be accurate to ± 0.1 ml. of 0.1 *N* sodium hydroxide per 100 ml., or ± 0.1 gram-equivalent per cubic metre.

The complete figures obtained in the examination of the various samples of in-shore water are given below.

STATION 1. OFF EAST COAST OF SCOTLAND, OPPOSITE ABERDEEN

Date: 24.12.38.

Time of high water at Aberdeen: 2.42 p.m.

Position	Time	State of tide	Salinity, g./1000 g.	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
57° 21' 15" N. 1° 54'	W. 1.50 p.m.	Springs	34.47	1.12	67.4
57° 19' 20" N. 1° 59'	W. 2.10 p.m.		34.42	0.68	67.4
57° 17' N. 1° 59'	W. 2.30 p.m.	Tidal stream setting	34.42	0.75	67.3
57° 14' 30" N. 2° 01' 30" W.	2.50 p.m.	South during this	33.96*	0.68	66.5
57° 12' N. 2° 03'	W. 3.10 p.m.	period. Reversal of	33.63*	0.68	65.7
57° 08' 20" N. 2° 03'	W. 3.30 p.m.	flow about 4 p.m.	33.95*	0.72	66.4

* Samples taken after high water at Aberdeen show a decrease in salinity.

STATION 2. $\frac{1}{4}$ MILE OFF MOUTH OF RIVER YTHAN, ABOUT 15 MILES NORTH OF ABERDEEN

Sample No.	Date	Time	Time of high water at Aberdeen	State of tide	Salinity, g./1000 g.	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
125	26.12.38	2.30 p.m.	3.50 p.m.	High water	33.52	0.86	65.5
126	26.12.38	9.00 p.m.	—	Low "	13.59	1.44	25.1
127	27.12.38	10.00 a.m.	—	Low "	11.53	1.51	21.7
128	27.12.38	4.30 p.m.	4.28 p.m.	High "	33.54	0.83	65.7
129	28.12.38	11.00 a.m.	—	Low "	11.60	0.92	21.7
130	28.12.38	4.30 p.m.	5.12 p.m.	High "	34.06	0.89	66.1
131	29.12.38	12.00 noon	6.03 p.m.	Low "	11.74	1.14	21.5
133	30.12.38	6.00 a.m.	6.53 a.m.	High "	5.48?	0.93?	9.8?
134	30.12.38	12.00 noon	—	Low "	31.66?	0.87?	61.6?

NOTES—(1) The low values of the salinity of the samples taken at low water show the influence of the river. The opposite results for Samples No. 133–134 suggest that these samples were wrongly labelled.

(2) The salinities at high water are rather lower than those obtained from Station 1.

STATION 3. OFF ABERDOUR BAY, MORAY FIRTH, POSITION 57° 41' N., 2° 11' W.

Date	Time	Time of high water at Aberdeen	State of tide	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
29.11.38	5.10 a.m.	5.56 a.m.	High water	34.37	2.58	2.2	0.52	67.4
29.11.38	11.12 a.m.		Low "	34.26	2.68	2.3	0.50	67.1
29.11.38	5.12 p.m.	5.55 p.m.	High "	34.32	2.63	2.2	0.50	67.3
29.11.38	11.10 p.m.		Low "	34.38	2.62	2.2	0.47	67.5
30.11.38	6.07 a.m.		High "	34.44	2.60	2.2	0.50	67.5
30.11.38	12.10 p.m.		Low "	34.48	2.69	2.3	0.47	67.6
30.11.38	6.10 p.m.	6.53 p.m.	High "	34.42	2.69	2.3	0.47	67.5
1.12.38	12.11 a.m.		Low "	34.53	2.69	2.3	0.49	67.7

STATION 4. OFF PORT KNOCKIE, MORAY FIRTH, POSITION 57° 42' 35" N., 2° 51' 35" W.

Sample No.	Date	Time	Time of high water at Aberdeen	State of tide	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Chlorine demand, g. of chlorine per cubic metre	Bromine, g./cubic metre
18	15.11.38	5.57 a.m.	7.01 a.m.	High water	30.01	2.48	2.1	0.53	Less than 2.6	58.5
19	15.11.38	11.15 a.m.		Low "	31.44	2.49	2.1	0.49	" 2.0	61.3
19A	15.11.38	12.05 p.m.		Low "	32.02				"	
20	15.11.38	6.30 p.m.	7.25 p.m.	High "	30.53	2.44	2.1	0.42	" 2.2	59.2
21	16.11.38	12.45 a.m.		Low "	32.96	2.60	2.2	0.43	" 1.4	64.7
22	16.11.38	7.09 a.m.	8.20 a.m.	High "	33.20	2.43	2.1	0.45	" 1.4	65.0
23	16.11.38	1.30 p.m.		Low "	34.04	2.55	2.2	0.47	" 1.2	66.6
24	16.11.38	7.30 p.m.	8.35 p.m.	High "	34.19	2.60	2.2	0.56	" 1.2	66.8

NOTES—(1) Either sample No. 19 or 19A appears to have been wrongly labelled. One of these samples was probably taken about midnight of the 14-15.11.38
 (2) The low salinities and high chlorine demand of samples No. 18, 19 and 20 may indicate contamination by river water.

STATION 5. OFF HOPEMAN, MORAY FIRTH, POSITION 57° 43' 30" N., 3° 26' W.

Date	Time	Time of high water at Aberdeen	State of tide	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Chlorine demand, g. of chlorine per cubic metre	Bromine, g./cubic metre
8.11.38	6.00 a.m.		Low water	33.25	2.76	2.4	0.67	Less than 1.4	65.0
8.11.38	11.55 a.m.	1.17 p.m.	High "	33.26	2.73	2.4	0.58	" 1.4	65.0
8.11.38	6.00 p.m.		Low "	32.57	2.73	2.4	0.57	" 1.4	63.8
9.11.38	12.07 a.m.	1.30 a.m.	High "	32.95	2.67	2.3	0.55	" 1.4	64.3
9.11.38	6.15 a.m.		Low "	33.59	2.67	2.3	0.46	" 1.2	65.3
9.11.38	12.33 p.m.	1.55 p.m.	High "	33.83	2.68	2.3	0.55	" 1.2	66.4
9.11.38	6.00 p.m.		Low "	34.20	2.67	2.3	1.25	" 0.8	67.0
21.11.38	5.30 a.m.	12.40 p.m.	High "	33.28	2.61	2.2	0.37	" 1.0	65.3
21.11.38	11.23 a.m.		Low "	33.34	2.61	2.2	0.40	" 1.3	66.3
21.11.38	5.30 p.m.		High "	33.44	2.95	2.3	0.45	" 1.3	66.5

STATION 6. RUDH'RE, WEST COAST OF SCOTLAND

Samples taken $\frac{1}{4}$ to $\frac{1}{2}$ mile off-shore

Date	Time	Time of high water at Gairloch	State of tide	Salinity, g./1000 g.	Bromine, g./cubic metre
29.12.38	10.00 a.m.	11.07 a.m.	High water. Neaps	34.08	66.7
29.12.38	4.00 p.m.		Low "	34.12	66.7
7.1.39	7.30 a.m.	7.19 a.m.	High "	33.80	66.8
7.1.39	1.30 p.m.		Low "	34.01	66.6
9.1.39	9.00 a.m.	8.58 a.m.	High " Springs	34.22	67.0
9.1.39	3.00 p.m.		Low "	34.23	67.0
10.1.39	9.45 a.m.	9.46 a.m.	High "	33.83	66.1
10.1.39	3.45 p.m.		Low "	34.25	66.9
11.1.39	10.00 a.m.	10.35 a.m.	High "	34.22	66.9
11.1.39	4.00 p.m.		Low "	34.28	66.9
12.1.39	10.45 a.m.	11.27 a.m.	High "	34.23	66.9
12.1.39	4.45 p.m.		Low "	33.89	65.8
14.1.39	8.00 a.m.		Low "	34.18	66.8
14.1.39	2.15 p.m.	1.44 p.m.	High "	34.18	66.2
16.1.39	10.00 a.m.		Low "	34.18	66.4
16.1.39	4.15 p.m.	4.12 p.m.	High " Neaps	34.20	66.8
17.1.39	11.00 a.m.		Low "	34.16	66.7
17.1.39	5.00 p.m.	5.03 p.m.	High "	34.22	66.8
18.1.39	11.45 a.m.		Low "	34.16	66.6
18.1.39	5.45 p.m.	5.49 p.m.	High "	34.23	66.2
19.1.39	6.00 a.m.			34.19	66.2
19.1.39	12.00 noon			34.22	66.6
20.1.39	12.45 p.m.		Low "	34.17	66.2
20.1.39	7.00 p.m.	6.54 p.m.	High "	34.02	66.2
21.1.39	7.45 a.m.	7.11 a.m.	High " Springs	33.73	65.4
21.1.39	2.00 p.m.		Low "	33.77	66.5

STATION 10 BARDSEY ISLAND, NORTH WALES

Date	Time	Time of high water at Bardsey	State of tide	Salinity, g./1000 g.	Bromine, g./cubic metre
6.1.39	H.W.	7.48 a.m.	} Springs	34.43	67.0
6.1.39	L.W.			34.46	67.1
7.1.39	H.W.	8.35 a.m.		34.49	67.1
7.1.39	L.W.			34.48	66.9
8.1.39	H.W.	9.24 a.m.		34.54	67.3
8.1.39	L.W.			34.51	67.3
13.1.39	9.00 a.m.		} Neaps	34.26	67.0
13.1.39	2.00 p.m.	1.47 p.m.		34.26	67.0
14.1.39	9.00 a.m.			34.30	67.1
14.1.39	3.00 p.m.	3.00 p.m.		34.13	66.8
16.1.39	L.W.			33.00	64.4
16.1.39	4.00 p.m.	5.28 p.m.		33.32	65.0

STATION 7. MACHRIHANISH, MULL OF KINTYRE, WEST COAST OF SCOTLAND

Samples taken $\frac{1}{4}$ mile off-shore

Date	Time	Time of high water at Campbeltown	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
12.12.38	6.30 a.m.	2.52 a.m.	33.57	2.60	2.2	0.33	65.7
12.12.38	12.00 noon	3.26 p.m.	33.26	2.75	2.4	0.35	65.2
13.12.38	7.00 a.m.	3.48 a.m.	33.59	2.81	2.4	0.38	65.7
13.12.38	12.30 p.m.	4.25 p.m.	33.32	2.84	2.5	0.33	65.1
14.12.38	7.30 a.m.	4.50 a.m.	33.40	2.85	2.5	0.40	65.3
14.12.38	1.00 p.m.	5.35 p.m.	33.62	2.86	2.5	0.36	65.7
15.12.38	8.00 a.m.	6.04 a.m.	33.69	2.70	2.3	0.40	65.9
15.12.38	1.30 p.m.	6.45 p.m.	33.53	2.72	2.3	0.44	65.5
16.12.38	8.30 a.m.	7.14 a.m.	33.50	2.71	2.3	0.56	65.7
16.12.38	2.00 p.m.	7.55 p.m.	33.62	3.05	2.7	0.50	65.6
19.12.38	7.00 a.m.	10.15 a.m.	33.54			0.54	65.9
19.12.38	1.00 p.m.	10.42 p.m.	33.53			0.55	65.6
20.12.38	7.30 a.m.	11.00 a.m.	33.24			2.92	65.1
20.12.38	1.30 p.m.	11.22 p.m.	33.27			0.60	65.3
21.12.38	8.00 a.m.	11.37 a.m.	33.22			0.59	64.7
21.12.38	2.00 p.m.	11.59 p.m.	33.43			0.70	65.4
22.12.38	8.30 a.m.	11.12 p.m.	33.35			0.51	65.4
22.12.38	2.30 p.m.	12.31 a.m.	33.52			0.51	65.8
23.12.38	9.00 a.m.	0.48 p.m.	33.32			0.51	65.1
23.12.38	3.00 p.m.	1.03 a.m.	33.49			0.55	65.4
26.12.38	10.00 a.m.	2.10 a.m.	33.39			0.50	65.0
26.12.38	4.00 p.m.	2.34 p.m.	33.18			0.53	64.6
27.12.38	10.45 a.m.	2.44 a.m.	33.41			0.54	65.0
27.12.38	4.45 p.m.	3.07 p.m.	33.20			1.03	64.7
28.12.38	11.30 a.m.	3.18 a.m.	33.05			0.55	64.4
28.12.38	5.30 p.m.	3.45 p.m.	33.26			0.61	64.7
29.12.38	6.30 a.m.	3.56 a.m.	33.05			0.59	64.4
29.12.38	12.30 p.m.	4.31 p.m.	33.39			0.61	65.0
30.12.38	7.15 a.m.	4.53 a.m.	33.43			0.56	64.8
30.12.38	1.15 p.m.	5.37 p.m.	33.46			0.58	64.9
2.1.39	6.30 a.m.	8.26 a.m.	32.90				64.2
2.1.39	12.00 noon	9.04 p.m.	32.71				63.4
3.1.39	7.00 a.m.	9.24 a.m.	33.17				64.6
3.1.39	12.30 p.m.	9.59 p.m.	33.21				64.7
4.1.39	7.30 a.m.	10.18 a.m.	33.38				65.2
4.1.39	1.00 p.m.	10.50 p.m.	33.39				65.1
5.1.39	8.00 a.m.	11.08 a.m.	33.43				65.3
5.1.39	1.30 p.m.	11.36 p.m.	33.31				65.2
6.1.39	8.30 a.m.	11.56 a.m.	33.06				64.6
6.1.39	2.00 p.m.	12.23 a.m.	33.27				65.1

STATION 8. OFF CORSEWALL POINT

Samples taken from S.S. *Princess Maud*, outward bound from Stranraer, with Corsewall Point abeam

Date	Time	Time of high water at Stranraer	State of tide	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Chlorine demand, g. of chlorine per cubic metre	Bromine, g./cubic metre
9.11.38	6.54 a.m.	0.02 a.m.	Springs	33.22	2.65	2.3	0.69	Less than 1.4	65.0
10.11.38	6.35 a.m.	0.37 a.m.	Ebb	33.49	2.65	2.3	0.67	"	65.7
11.11.38	6.51 a.m.	1.18 a.m.		33.31	2.58	2.2	0.65	"	65.2
12.11.38	6.51 a.m.	2.05 a.m.		33.64	2.78	2.4	0.74	"	66.0
14.11.38	7.08 a.m.	3.54 a.m.	Neaps	33.33	2.76	2.4	0.77	"	65.1
15.11.38	6.49 a.m.	5.13 a.m.		33.64	2.70	2.3	0.60	"	66.1
16.11.38	6.50 a.m.	6.31 a.m.		33.68	2.75	2.4	0.47	"	66.0
17.11.38	6.50 a.m.	7.40 a.m.	Flood	33.59	2.77	2.4	0.53	"	65.7
18.11.38	7.08 a.m.	8.43 a.m.		33.58	2.75	2.4	0.58	"	65.7
19.11.38	6.59 a.m.	9.39 a.m.		33.57	2.63	2.3	0.61	"	65.6
21.11.38	6.51 a.m.	11.08 a.m.	Springs	33.67	2.60	2.2	0.63	"	65.8
22.11.38	7.20 a.m.	11.44 a.m.		33.45	2.57	2.2	0.52	"	65.5
30.11.38	6.52 a.m.	4.49 a.m.		33.60	3.05	2.7	0.58	"	65.6
1.12.38	7.51 a.m.	6.03 a.m.	Neaps	33.64	2.85	2.5	0.53	"	65.8
2.12.38	6.55 a.m.	7.13 a.m.		33.72	2.83	2.5	0.56	"	65.8
3.12.38	7.00 a.m.	8.12 a.m.		33.58	2.87	2.5	0.71	"	65.8
5.12.38	6.53 a.m.	9.48 a.m.	Flood	33.26	2.85	2.5	0.77	"	65.2
6.12.38	7.30 a.m.	10.34 a.m.		33.34	2.98	2.6	0.58	"	65.0
7.12.38	6.57 a.m.	11.17 a.m.		33.23	2.58	2.2	0.74	"	64.6
8.12.38	7.30 a.m.	12.02 p.m.	Springs	33.03	2.67	2.3	1.07	"	64.3
9.12.38	7.21 a.m.	12.47 p.m.		33.18	2.64	2.3	0.72	"	64.8
10.12.38	7.30 a.m.	1.07 a.m.		33.04	2.58	2.2	0.73	"	64.4
12.12.38	6.53 a.m.	2.48 a.m.	Ebb	33.25	2.62	2.2	0.73	"	64.8
13.12.38	6.52 a.m.	3.44 a.m.		33.09	2.65	2.3	0.72	"	64.8
20.12.38	7.56 a.m.	10.54 a.m.		33.12	2.62	2.3	0.62	"	64.4
21.12.38	8.19 a.m.	11.33 a.m.	Flood	33.15	2.62	2.3	0.65	"	64.9
22.12.38	7.21 a.m.	12.08 p.m.		33.15	2.62	2.3	0.62	"	64.9
23.12.38	8.50 a.m.	12.44 p.m.		33.24	2.62	2.3	0.65	"	65.0
24.12.38	10.01 a.m.	1.20 p.m.	Springs	32.95	2.62	2.2	0.80	"	64.5
26.12.38	7.14 a.m.	2.06 a.m.		32.98	2.62	2.2	0.68	"	64.6
27.12.38	6.48 a.m.	2.40 a.m.		32.87	2.62	2.2	0.80	"	64.4
28.12.38	7.15 a.m.	3.14 a.m.	Ebb	32.95	2.62	2.2	0.65	"	64.4
29.12.38	7.30 a.m.	3.52 a.m.		32.84	2.62	2.2	0.62	"	64.1
30.12.38	7.30 a.m.	4.49 a.m.		32.91	2.62	2.2	0.65	"	64.3
31.12.38	7.24 a.m.	5.57 a.m.	Neaps	32.85	2.62	2.2	0.65	"	63.9
2.1.39	6.54 a.m.	8.22 a.m.		32.71	2.62	2.2	0.65	"	63.5

STATION 9. OFF SOUTH STACK, ANGLESEY
 Samples taken from L.M.S. mail steamers, outward or inward bound from Holyhead with South Stack abeam

Date	Time	Time of high water at Holyhead	State of tide	Temperature, °C.	Salinity, g./1000 g.	0.1 N H ₂ SO ₄ required per 100 ml. of sea-water to give pH 3.5, ml.	Calculated excess base, g.-equiv. per cubic metre	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Chlorine demand, g. of chlorine per cubic metre	Bromine, g./cubic metre
9.11.38	2.51 p.m.	10.45 a.m.	Springs	12.8	33.84	2.69	2.3	0.55	Less than 1.4	66.3
9.11.38	11.40 p.m.	11.05 p.m.		12.2	33.72	2.68	2.3	0.52	"	66.3
10.11.38	2.52 p.m.	11.28 a.m.		12.2	33.88	2.67	2.3	0.47	"	66.0
10.11.38	11.29 p.m.	11.49 p.m.		11.7	33.78	2.66	2.3	0.50	"	65.9
11.11.38	2.59 p.m.	0.15 p.m.		12.8	33.96	2.71	2.3	0.43	"	66.2
11.11.38	11.42 p.m.	0.37 a.m.		12.2	33.77	2.78	2.4	0.37	"	65.8
15.11.38	3.23 a.m.	4.07 a.m.		12.2	33.89	2.55	2.2	0.05	"	66.4
15.11.38	11.44 a.m.	4.32 p.m.		12.2	33.91	2.65	2.3	0.20	"	65.7
16.11.38	3.18 a.m.	5.20 a.m.		12.8	33.83	2.66	2.3	0.12	"	66.5
16.11.38	11.46 a.m.	5.49 p.m.		12.8	33.78	2.66	2.3	0.26	"	66.1
30.11.38	3.22 a.m.	3.36 a.m.	Neaps	10.6	33.77	2.76	2.4	0.12	"	65.5
1.12.38	3.18 a.m.	4.38 a.m.		11.1	33.96	2.82	2.4	0.10	"	66.2
1.12.38	11.48 a.m.	5.09 p.m.		10.0	33.92	2.58	2.2	0.47	"	65.9
2.12.38	3.22 a.m.	5.45 a.m.		10.0	34.02	2.90	2.5	0.20	"	66.3
2.12.38	11.46 a.m.	6.03 p.m.		10.6	34.12	2.82	2.4	0.54	"	66.3
8.12.38	2.54 p.m.	10.34 a.m.		11.1	34.08	2.85	2.5	0.59	"	66.5
8.12.38	11.23 p.m.	10.55 p.m.		9.4	33.80	2.89	2.5	0.18	"	65.8
9.12.38	7.37 a.m.	11.18 a.m.		8.9	33.62	2.68	2.3	0.30	"	65.3
9.12.38	2.19 p.m.	11.42 p.m.		9.4	33.79	2.75	2.4	0.21	"	66.0
6.1.39	3.40 p.m.	10.22 a.m.		10.0	33.75	2.71	2.3	0.30	"	65.7
6.1.39	11.54 p.m.	10.45 p.m.	6.7	33.61	2.71	2.3	0.30	"	65.9	
7.1.39	2.54 p.m.	11.08 a.m.	7.2	33.85	2.85	2.5	0.18	"	65.7	
7.1.39	11.38 p.m.	11.30 p.m.	7.8	33.59	2.85	2.5	0.18	"	65.7	
14.1.39	3.21 a.m.	4.59 a.m.	8.3	33.85	2.85	2.5	0.18	"	66.0	
14.1.39	11.45 a.m.	5.32 p.m.	7.2	33.68	2.85	2.5	0.18	"	65.6	
15.1.39	3.38 a.m.	6.17 a.m.	8.3	33.87	2.85	2.5	0.18	"	66.3	
15.1.39	11.35 p.m.	6.50 p.m.	8.3	33.64	2.85	2.5	0.18	"	65.8	
16.1.39	2.54 p.m.	7.34 a.m.	8.9	34.05	2.85	2.5	0.18	"	66.5	
16.1.39	11.27 p.m.	7.58 p.m.	8.3	34.04	2.85	2.5	0.18	"	66.4	
16.1.39			8.3	34.00	2.85	2.5	0.18	"	66.3	

STATION 11. OFF STRUMBLE HEAD, PEMBROKESHIRE

Samples taken from S.S. *St. David* outward bound from Fishguard with Strumble Head abeam

Date	Time	Time of high water at Fishguard	State of tide	Temperature, ° C.	Salinity, g./1000 g.	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
1.12.38	2.50 a.m.	1.18 a.m.	Neaps	11.2	34.82	0.90	67.8
2.12.38	2.45 a.m.	2.28 a.m.		11.1	34.69	0.74	67.8
3.12.38	2.50 a.m.	3.27 a.m.	Flood	11.3	34.71	0.68	67.8
4.12.38	3.00 a.m.	4.16 a.m.		11.2	34.71	2.01	67.8
6.12.38	2.30 a.m.	5.49 a.m.	Springs	11.1	34.77	0.91	68.0
7.12.38	3.00 a.m.	6.32 a.m.		11.0	34.77	0.77	67.8
8.12.38	2.30 a.m.	7.17 a.m.	Springs	11.0	34.79	0.32	67.8
9.12.38	3.00 a.m.	8.02 a.m.		10.8	34.80	0.74	68.0
10.12.38	2.50 a.m.	8.51 a.m.	Ebb	10.8	34.73	0.85	68.0
11.12.38	3.05 a.m.	9.43 a.m.		11.0	34.71	0.79	68.0
13.12.38	2.50 a.m.	11.36 a.m.	Ebb	11.0	34.84	0.97	68.1
14.12.38	3.00 a.m.	0.01 a.m.		11.3	34.84	0.85	68.2
15.12.38	3.00 a.m.	1.15 a.m.	Neaps		34.90	0.61	67.8
16.12.38	3.00 a.m.	2.25 a.m.				34.83	0.59
17.12.38	3.30 a.m.	3.35 a.m.	Flood		34.74	0.55	67.8
18.12.38	4.35 a.m.	4.32 a.m.				34.92	0.57
20.12.38	3.45 a.m.	6.11 a.m.	Springs		34.52	0.57	67.7
21.12.38	4.00 a.m.	6.48 a.m.				34.83	0.68
23.12.38	3.00 a.m.	7.59 a.m.	Flood		33.94	0.62	66.5
24.12.38	7.00 a.m.	8.35 a.m.				34.13	0.69
25.12.38	3.30 a.m.	9.11 a.m.	Springs		34.22	0.60	66.8
28.12.38	2.40 a.m.	10.56 a.m.				34.28	1.13
28.12.28	2.40 a.m.	10.56 a.m.	Ebb	8.3	34.23		66.8
29.12.38	2.30 a.m.	11.42 a.m.			8.5	34.12	
30.12.38	2.50 a.m.	0.04 a.m.	Neaps	8.1	33.92		66.1
31.12.38	2.30 a.m.	1.12 a.m.			8.1	33.92	
1.1.39	3.00 a.m.	2.25 a.m.	Neaps	8.7	33.95		66.4
3.1.39	2.30 a.m.	4.35 a.m.			8.5	34.25	
4.1.39	2.40 a.m.	5.29 a.m.	Flood	8.0	33.93		66.3
4.1.39	2.40 a.m.	5.29 a.m.			8.0	33.96	
5.1.39	2.20 a.m.	6.19 a.m.	Springs	7.6	33.78		66.0
6.1.39	2.35 a.m.	7.07 a.m.			8.1	33.94	
7.1.39	2.20 a.m.	7.54 a.m.	Springs	8.5	34.05		66.4
8.1.39	3.00 a.m.	8.43 a.m.			8.8	34.09	
10.1.39	2.30 a.m.	10.21 a.m.	Ebb	9.1	34.39		67.3
11.1.39	2.45 a.m.	11.10 a.m.			9.1	34.32	
11.1.39	2.45 a.m.	11.10 a.m.	Ebb	9.1	34.30		66.7
12.1.39	2.30 a.m.	0.02 p.m.			8.5	34.22	
13.1.39	2.30 a.m.	0.27 a.m.	Neaps	8.6	34.26		66.8
14.1.39	2.30 a.m.	1.33 a.m.			8.7	34.33	
15.1.39	2.50 a.m.	2.56 a.m.	Neaps	9.2	34.33		66.9
17.1.39	2.40 a.m.	5.10 a.m.			9.3	34.51	
18.1.39	2.30 a.m.	5.58 a.m.	Flood	9.3	34.60		67.4
18.1.39	2.30 a.m.	5.58 a.m.			9.3	34.58	
19.1.39	2.30 a.m.	6.40 a.m.	Flood	9.4	34.54		67.3
20.1.39	2.30 a.m.	7.13 a.m.			9.3	34.47	
21.1.39	2.30 a.m.	7.45 a.m.	Springs	9.6	34.58		67.4
22.1.39	3.15 a.m.	8.15 a.m.			9.3	34.57	
24.1.39	2.30 a.m.	9.24 a.m.	Ebb	9.0	34.73		67.8
25.1.39	2.30 a.m.	9.56 a.m.			8.9	34.65	
25.1.39	2.30 a.m.	9.56 a.m.	Ebb	8.9	34.67		67.7
26.1.39	3.15 a.m.	10.25 a.m.			9.0	34.66	
27.1.39	3.15 a.m.	11.00 a.m.	Ebb	8.7	34.56		67.1
28.1.39	2.30 a.m.	11.45 a.m.			8.6	34.62	
29.1.39	3.00 a.m.	0.11 a.m.	Neaps	8.5	34.43		67.1
31.1.39	2.30 a.m.	2.52 a.m.			8.0	34.52	

STATION 12

SENNEN COVE, LAND'S END (LIFEBOAT SLIPWAY)

Date	Time	Time of high water at Penzance	State of tide	Salinity, g./1000 g.	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre
16.12.38	11.30 a.m.	11.59 a.m.		34.99		68.6
16.12.38	1.30 p.m.			35.04		68.8
17.12.38	12.40 p.m.	1.08 p.m.		34.97		68.3
17.12.38	2.40 p.m.			34.98		68.5
18.12.38	1.40 p.m.	2.06 p.m.		34.85		68.2
19.12.38	3.27 p.m.	3.00 p.m.		34.99	0.66	68.4
20.12.38	4.10 p.m.	3.45 p.m.		34.97	0.66	68.3
21.12.38	Noon	4.22 p.m.		34.84		68.4
14.1.39	1 hr. before H.W.			35.07		68.6
14.1.39	H.W.	11.07 a.m.		35.01		68.4
14.1.39	1 hr. after H.W.			34.85		68.2
14.1.39	1 hr. before L.W.		Neaps	34.66		67.8
14.1.39	L.W.			34.74		68.0
14.1.39	1 hr. after L.W.			34.85		66.9
21.1.39	1 hr. before H.W.			35.02		68.5
21.1.39	H.W.	5.20 p.m.		35.07		68.4
21.1.39	1 hr. after H.W.			35.02		68.1
21.1.39	1 hr. before L.W.		Springs	35.01		68.3
21.1.39	L.W.			34.88		68.0
21.1.39	1 hr. after L.W.			34.97		68.2

CUMBERLAND

Place	Date	Time	Place for high water	Time of high water	Salinity, g./1000 g.	Bromine, g./cubic metre	Remarks
Maryport	27.2.39	2.30 p.m.	Maryport	4.33 p.m.	23.62	46.1	Opposite Rischow Farm
"	29.2.39	1.30 p.m.	"	"	22.29	43.5	Inner dock
"	29.2.39	1.55 p.m.	"	"	23.31	45.5	Entrance to harbour
St. Helens	27.2.39	3.05 p.m.	"	4.33 p.m.	24.87	48.6	3 miles north of Workington
Harrington	27.2.39	4.20 p.m.	Harrington	4.22 p.m.	29.42	57.5	North side
Whitehaven	28.2.39	9.05 a.m.	Whitehaven	5.01 a.m.	30.32	59.6	Outside north sea wall of harbour
St. Bees	28.2.39	10.45 a.m.	"	5.41 p.m.	29.70	58.0	2½ miles south of St. Bees, below Coulderton
Seascale	28.2.39	1.30 p.m.	"	5.41 p.m.	28.64	55.9	Foreshore, north side
"	28.2.39	5.05 p.m.	"	5.41 p.m.	30.08	58.8	Foreshore
Stub Place	28.2.39	3.00 p.m.	"	5.41 p.m.	30.95	60.5	North-east of Bootle

NORTH WALES

Place	Date	Time	Place for high water	Time of high water	Salinity, g./1000 g.	Bromine, g./cubic metre	Remarks
Amlwch Harbour	20.2.39	11.50 a.m.	Amlwch Harbour	11.11 a.m.	31.89	62.3	Inside first basin
Holyhead	20.2.39	8.50 a.m.	"	11.03 a.m.	33.78	66.1	At neck of land near harbour office
Treaddur Bay	20.2.39	9.45 a.m.	"	11.03 a.m.	33.96	66.4	Off north end of beach
"	20.2.39	10.00 a.m.	"	11.03 a.m.	33.89	66.2	Between Treaddur Bay and Porthy Post
Four Mile Bridge	20.2.39	9.20 a.m.	Holyhead	11.03 a.m.	31.94	62.4	Northerly rush of water through small opening in bridge. Taken in stream
Beddmanarch Bay	20.2.39	10.25 a.m.	"	11.03 a.m.	33.40	65.3	South-west corner. Off rocks by road
Waterloo Port	20.2.39	2.30 p.m.	"	11.03 a.m.	32.50	63.5	"
Pwllhelli	20.2.39	3.50 p.m.	"	8.48 a.m.	31.85	62.2	Careg yr Imbill
Aberch	2.3.39	2.50 p.m.	"	"	24.31	47.5	At Railway Station
"	2.3.39	2.50 p.m.	Pwllhelli	"	24.11	47.1	At Railway Station
Afonwen	20.2.39	4.45 p.m.	"	8.48 a.m.	26.65	52.1	"
"	2.3.39	3.30 p.m.	"	"	29.63	57.9	"
Prestatyn	26.10.38	11.00 a.m.	"	12.20 p.m.	31.09	60.6	"
Rhyl	26.10.38	11.30 a.m.	"	12.20 p.m.	30.73	59.7	"
Abergele	26.10.38	12.10 a.m.	Rhyl	12.20 p.m.	31.40	61.3	"
Colwyn Bay	26.10.38	12.50 a.m.	"	12.20 p.m.	32.10	62.6	"

CORNWALL

Place	Date	Time	Place for high water	Time of high water	Salinity, g./1000 g.	Soluble phosphate, mg.-atoms of phosphorus per cubic metre	Bromine, g./cubic metre	Remarks	
Bass Rocks, east side	10.1.39	10.00 a.m.	Falmouth	7.53 a.m.	34.58		67.5	Taken from Quarry Jetty North side of pier Possible inlet on north side South side, <i>i.e.</i> , along side of pier Inshore end of Zarn Carve South-west corner near one of many inlets	
Parsons Cove	9.1.39	11.30 a.m.		7.05 a.m.	34.75		68.0		
West Coombe	9.1.39	11.00 a.m.		7.05 a.m.	34.27		66.7		
Forthoustock		66.7
Dean Quarries	2.1.39	2.30 p.m.		1.13 p.m.	35.07		68.6		
" "	35.12		
" "	10.1.39	10.55 a.m.	7.05 a.m.	33.80		65.8			
Downas Cove	2.1.39	11.30 a.m.	1.13 p.m.	34.35		67.3			
Kennack Sands	2.1.39	10.15 a.m.	1.13 p.m.	29.27		57.1			
Carleone Cove	1.1.39	3.30 p.m.	Lizard Pt.	12.01 p.m.	34.02		67.4	South side of cove. Considerable stream runs into centre of cove	
" "	1.1.39	3.30 p.m.		12.01 p.m.	29.55		57.4	North side of cove. Considerable stream runs into centre of cove	
Church Cove	1.1.39	11.30 a.m.		12.01 p.m.	33.63		65.6	Two small streams run into cove	
Kynance Cove	31.12.38	10.15 a.m.		10.48 a.m.	34.61		67.6	On foreshore	
Pestreach Cove 1	29.12.38	1.00 p.m.		9.38 a.m.	34.69		67.7	In natural culvert away from stream	
" 2	29.12.38	1.00 p.m.		9.38 a.m.	34.27		66.8	Outer edge of rocks near waterfall entering sea	
Marazion	2.1.39	4.30 p.m.	Penzance	1.11 p.m.	33.97		66.5	Head of Mount's Bay	
Mill Bay	16.12.38	9.45 a.m.		1.45 p.m.	34.18	0.56	66.9	Shore side of Flat Rock	
" "	16.12.38	10.15 a.m.		1.45 p.m.	35.00	0.53	68.7	Mouth of tunnel	
Whitesand Bay	14.12.38	12.00 noon		11.07 a.m.	35.08		68.6	Taken in surf clear of land water	
Portreath	7.1.39	12.00 noon		5.42 p.m.	34.51		67.5	Off rocks at end of pier at low water	
Chapel Porth	6.1.39	3.00 p.m.	St. Ives	4.55 p.m.	32.64		63.8		
Trevellas Porth	6.1.39	11.45 a.m.		4.55 p.m.	34.93		67.9		
" "	6.1.39	12.00 noon		4.55 p.m.	31.76		61.9	Near outfall of stream	
Perran Bay	5.1.39	2.15 p.m.		5.02 p.m.	34.94		68.2	North end	
Watergate Bay	5.1.39	11.00 a.m.	Padstow	5.02 p.m.	34.83		67.8	300 yd. of stream, 1 hr. after low tide	
Pulverton Bay	3.1.39	3.50 p.m.		3.24 p.m.	34.82		67.8	Little cove	
Harlyn Bay	3.1.39	3.00 p.m.		3.24 p.m.	34.58		67.6	On John Cove	
Manorbier Bay	19.1.39	4.15 p.m.	Tenby	5.36 p.m.	31.64		61.8	Away from dilution	
Freshwater East	20.1.39	10.00 a.m.		5.19 a.m.	25.72		49.7	South side, away from dilution	
Stacpole Quay	20.1.39	12.00 noon		5.19 a.m.	16.73		32.1	Possible dilution from stream	

PEMBROKESHIRE

Our survey confirmed the view that the water of highest salinity was to be found off the coast of Cornwall. The salinity decreases in the Irish Sea from Fishguard northwards, and then increases along the west coast of Scotland (owing, presumably, to fresh Atlantic water coming north of Ireland). The salinity is also fairly high off the east coast of Scotland away from river estuaries. The results of the salinity and bromine determinations showed that the ratio between the two is remarkably constant except when the water is seriously diluted with river water.

Ultimately, other considerations besides the amount of bromine in the sea-water led to the choice of Hayle, Cornwall, as the site for a bromine plant, but the information obtained in this survey was of considerable value.

The figures for salinity given in the charts were all determined by the Knudsen method, which is an exceedingly accurate method, as is shown by the results of the examination of three samples of sea-water which were carried out quite independently (*a*) at Winnington, Cheshire, and (*b*) at the Oceanographic Department of the University of Liverpool.

Sample	Result obtained at	Result obtained at the
	Winnington Salinity, g./1000 g.	Oceanographic Department, Liverpool Salinity, g./1000 g.
1	34.124	34.122
2	34.030	34.036
3	33.986	33.982

Nevertheless, the method takes appreciable time and comparatively large volumes of reagent are used, so that the method is not suitable for rapid surveys.

Working at Hayle, in Cornwall, we had to develop a rapid method of determination of the salinity of samples of sea-water, contaminated with river water, at 5-minute intervals throughout the day. The salinity varied with the state of the tide and other factors.

Five samples of sea-water, of widely different salinities, were first obtained from this source. Accurate determinations of the salinity of these waters were first made by the application of Knudsen's method, using Knudsen's sea-water as standard, with subsequent reference to Knudsen's tables. The salinities were as follows—

Sample	Salinity, g./1000 g.
A	35.1
B	31.6
C	29.0
D	24.7
E	20.7

Two lactometers were now obtained, No. 1 covering the range 1.015 to 1.025, and No. 2 covering the range 1.025 to 1.035. The lactometer readings of the five samples of sea-water were taken at three different temperatures, *viz.*, 10°, 15° and 20° C. From these readings Fig. 1 was constructed. This graph relates lactometer reading with temperature and salinity.

In the examination of samples, the lactometer reading is taken and the temperature measured; the salinity is then read directly from the graph. If necessary, a chain hydrometer may be substituted for the lactometer. In any case the rapid method gives results of appreciable accuracy, as is shown by the following figures—

Salinity by rapid method, g./1000 g.	Salinity by Knudsen's method, g./1000 g.
26.65	26.76
27.25	27.69
32.70	32.77
33.35	33.42
33.50	33.40
34.15	34.14
34.55	34.51
34.65	34.78
34.80	34.87
34.90	34.95
35.05	34.88

The bromine content of a sample of sea-water in g. of bromine per cubic metre of sample may be estimated with considerable accuracy by multiplying the figure for salinity (g. per 1000 g.) by the factor 1.956.

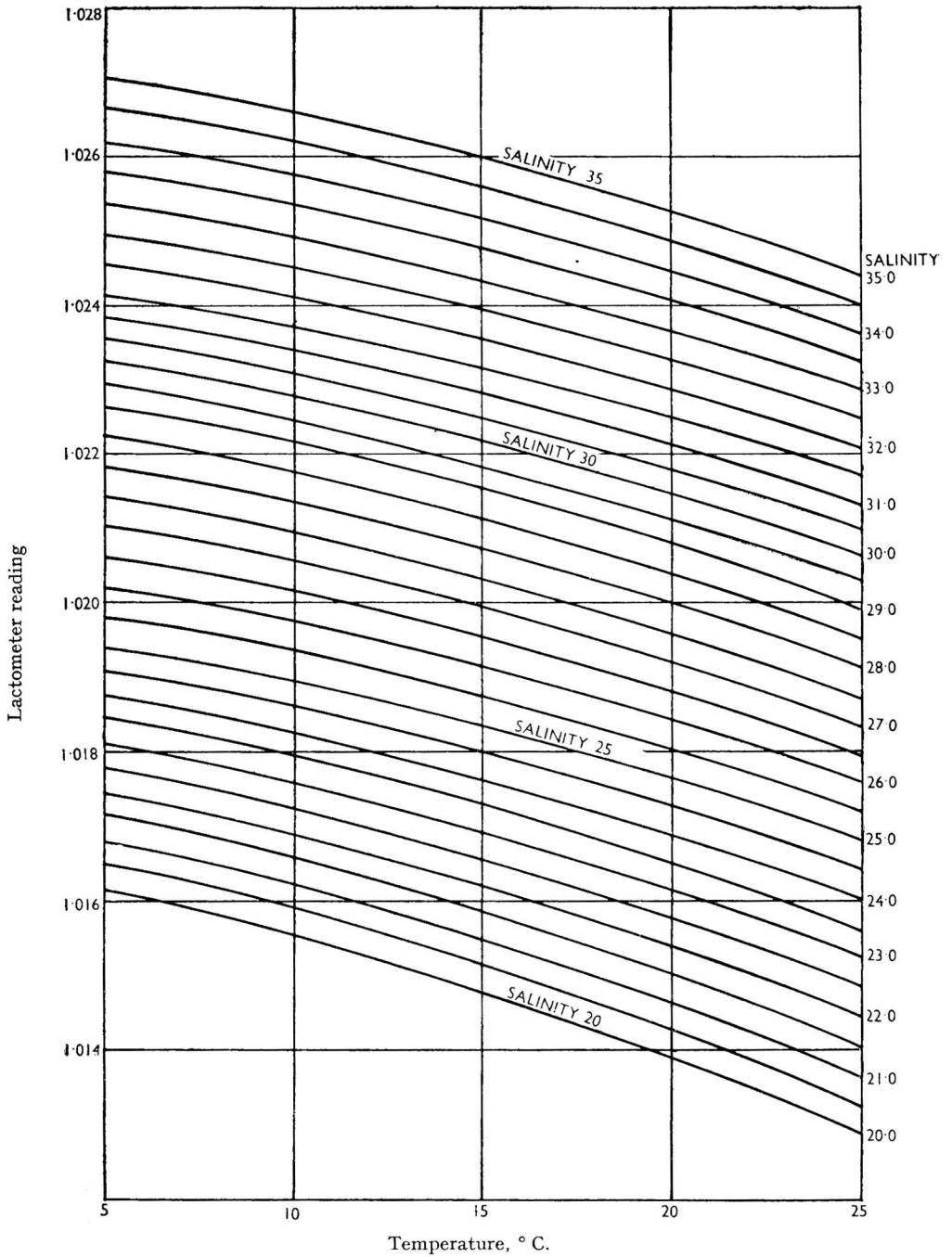


Fig. 1. Relationship between lactometer reading, temperature and salinity in g. per 1000 g.

Part IV. The Analysis of Bromine and Substances Containing Bromine

By J. HASLAM

SYNOPSIS—This paper is concerned with the determination of bromine and chlorine in acid solutions, and in solutions prepared by the action of bromine and chlorine on alkalis. The determination of bromine in such substances as ammonium chloride, calcium chloride, ethylene dibromide, as well as in air and urine, is discussed, and details are given of the method of determination of chlorine in bromine.

As a result of several years' work on the analysis of bromine and compounds containing bromine, many methods were tested, and the purpose of this paper is to place on record those methods found to be most successful. The methods are described under separate headings.

BROMINE

The following determinations are usually carried out—

1. *Sulphate*—About 5 ml. of the sample are placed in a beaker containing 50 ml. of water. The bromine is boiled off in a fume cupboard and the sulphate in the residual solution is determined by precipitation as barium sulphate.

2. *Residue on evaporation*—Three millilitres of the sample are allowed to evaporate spontaneously in a porcelain basin and the residue is weighed.

3. *Chlorine*—With samples of very crude bromine containing 5 to 10 per cent. of chlorine, a rough approximation to the amount of chlorine present may be obtained by weighing out, from a weight pipette, about 15 g. of the sample into a large volume of water contained in a litre flask. The sample is dissolved by prolonged shaking and the solution is diluted to the mark. By means of a pipette, 25 ml. of this solution are transferred into a solution of 5 g. of potassium iodide in 150 ml. of water, and the liberated iodine is titrated with 0.1 *N* sodium thiosulphate solution. The chlorine content of the sample is calculated from this titration on the assumption that the sample consists entirely of chlorine and bromine, although this assumption may not be entirely justifiable for impure samples.

An alternative and more accurate method, for samples of bromine containing appreciable proportions of chlorine, is to weigh out accurately about 3 g. of the sample into a small well-stoppered weighing bottle contained in a larger weighing bottle. The sample thus weighed is washed into about 25 ml. of a saturated solution of sulphur dioxide in water, which has been diluted to about 100 ml. with water. The excess of sulphur dioxide is then removed by prolonged boiling, and the solution is cooled and diluted to 200 ml. With a pipette, 25 ml. of this solution are taken and 2.5 g. of sodium nitrate (AnalaR) are added. This solution is then titrated potentiometrically with 0.1 *N* silver nitrate solution, using the calomel reference electrode and ammonium nitrate bridge as described on p. 376. The proportion of chlorine is deduced from the difference between the first and second end-points of the titration.

In the determination of chlorine in samples of purified bromine the apparatus is first assembled as shown in Fig. 1. Twenty-five millilitres of 0.1 *N* potassium bromide solution and 50 ml. of water are placed in flask A, and 5 ml. of the bromine sample are added from a burette. When the solution has stood for about half an hour, the excess of bromine is drawn off by means of a pump, and the last traces of bromine are removed by boiling the solution in the reaction flask. The residual solution is then cooled and diluted to 200 ml. with water.

A Volhard determination is carried out on 100 ml. of the dilute solution, and the Kolthoff and Yutzy method of determination of bromine is applied to 50 ml. of the dilute solution after addition of 15 g. of sodium chloride (AnalaR). A blank titration is carried out on 15 g. of sodium chloride (AnalaR).

The calculation of the amount of chlorine in the sample is based on the fact that the potassium bromide solution finally obtained in the test contains all the chlorine present

in the original 5 ml. of bromine, either as free chlorine or as chloride. The Kolthoff and Yutzy test gives the total bromine (as bromide) present in the final solution, and the difference between this figure and the total halide as determined in the Volhard test is a measure of the amount of chlorine present in the original 5 ml. of sample.

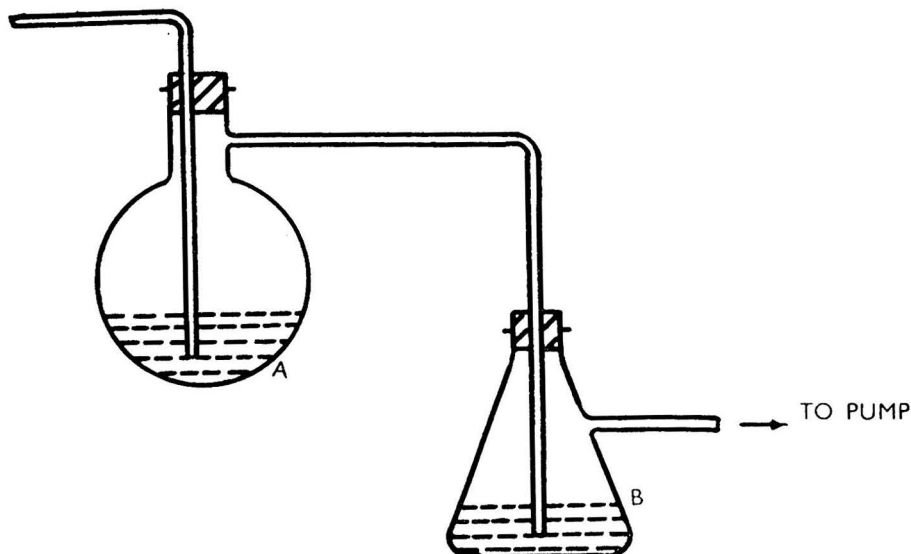


Fig. 1. Apparatus assembly

Flask A contains 25 ml. of 0.1 *N* potassium bromide, 50 ml. of water and 5 ml. of the bromine sample. Flask B contains sodium carbonate solution

In work of the highest accuracy in the determination of very small amounts of chlorine in bromine, we have carried out the preliminary treatment of 5 ml. or other suitable volume of the sample with 25 ml. of 0.1 *N* potassium bromide solution in the manner indicated above, but the final titration of the potassium chloride produced in the reaction has been carried out potentiometrically. If two similar electrodes are immersed in a solution which is being titrated and the arrangement is such that diffusion of solution around one electrode is prevented so that the concentration there is kept different from the concentration of reacting substance around the other electrode, a current will flow between the two electrodes when the circuit is completed and the maximum e.m.f. will be produced at the end-point.

Of the many devices on this principle, that of E. Müller¹ seemed to be most suited to our requirements. A diagram of Müller's retarded auxiliary electrode is given in Fig. 2. As described in the paper cited, the electrode system has two manifest disadvantages.

When the electrode is placed in the solution to be titrated, the capillary is filled by capillary attraction to a level slightly higher than the level in the titrating beaker. This necessarily removes from the sphere of the reaction a small volume of liquid, the exact amount of which will be governed by the bore of the capillary, the depth of immersion and the gauge of the silver wire inside the capillary. In the electrode system which we found most suitable the volume of liquid so removed was of the order of 0.1 ml., and although this can obviously be neglected in most titrations, it was felt that when a high order of accuracy was desired in the titration of small volumes of solution, action should be taken to avoid this source of error. This was effected by filling the capillary to the required level with a solution containing a small but definite concentration of silver ions before immersing the electrode in the solution to be titrated. The actual electrode solution is varied according to the particular electrometric titration being carried out.

The second defect inherent in the design of Müller's original electrode is that, as the top of the capillary is open, the level of liquid in the capillary will constantly rise during the course of the titration owing to the addition of the standard solution used in the titration. This causes an influx into the capillary of solution in which the concentration of the active

ion differs from that originally enclosed in the capillary. The metal wire inside the capillary is thus in contact with a solution in which the concentration of metallic ion is not constant throughout the course of the titration and irregularities may appear in the titration curve. We have overcome this defect by using a modified capillary as shown in Fig. 3.

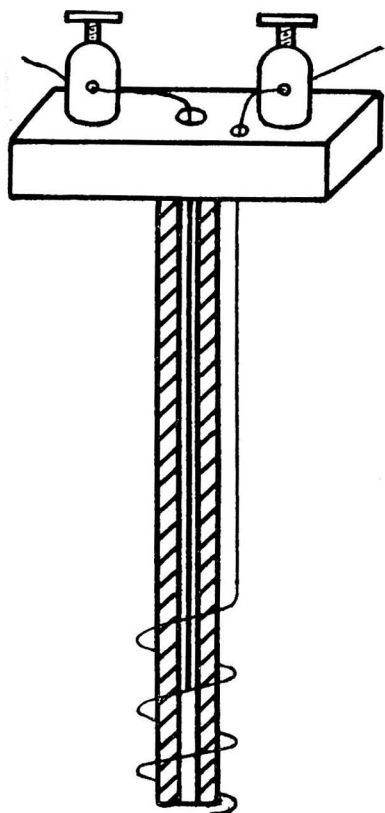


Fig. 2. Müller's capillary electrode

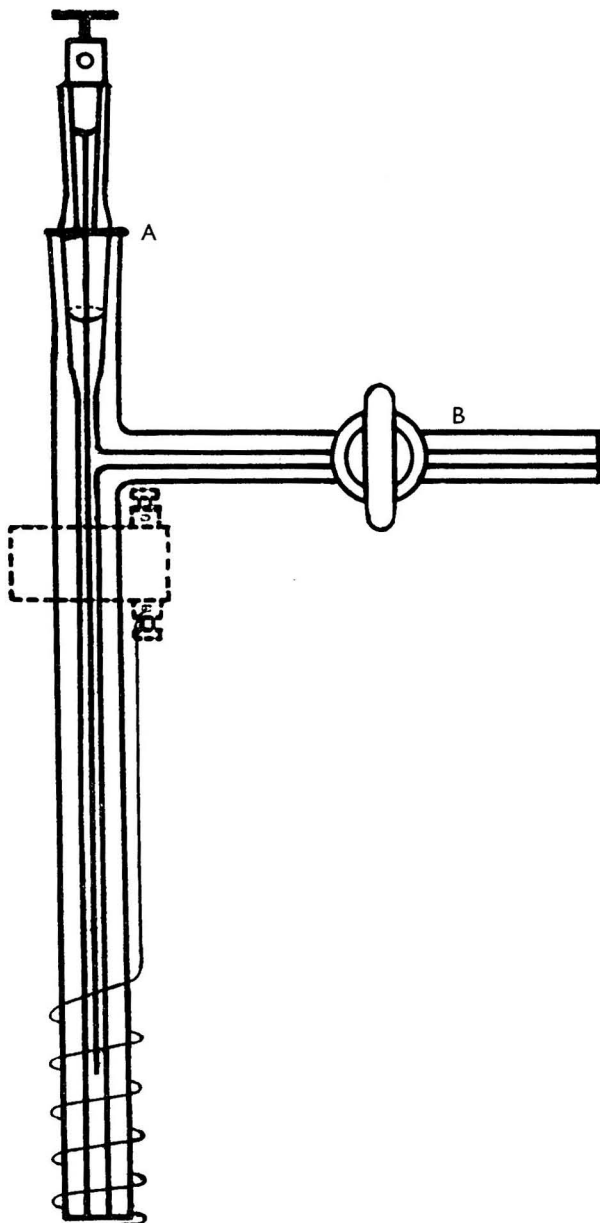


Fig. 3. Modified Müller electrode

A ground glass joint, A, carries the metal wire soldered to the terminal (which is rendered air-tight). The side-arm, B, is provided with a tap which is opened after the capillary has been immersed in a suitable electrode solution. The tap is then closed and the capillary withdrawn and rinsed externally with distilled water before being inserted in the coil of metal

wire which forms the other electrode. In all titrations of halide ions by means of silver nitrate, the electrodes consisted of No. 20 gauge fine silver wire; the internal diameter of the capillary was 1.0 mm. Fig. 4 shows the design of the holder used.

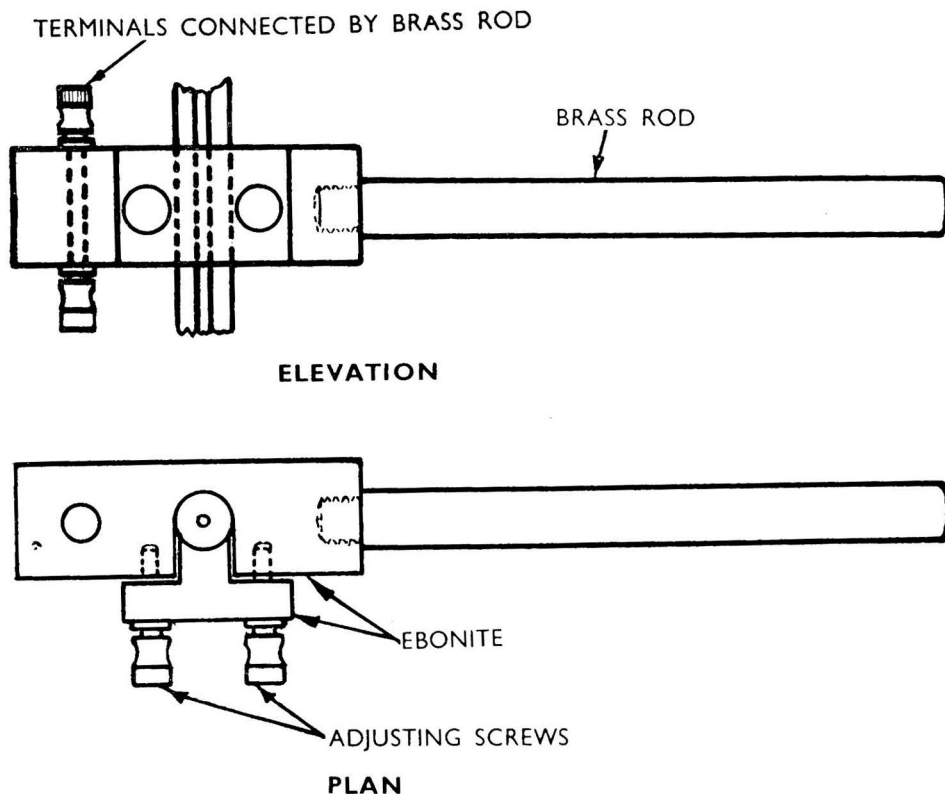


Fig. 4. Electrode holder

In the determination of small amounts of chlorine in bromine, the reaction liquid obtained after treatment of the 25 ml. of 0.1 *N* potassium bromide is titrated potentiometrically, after addition of 2.5 g. of sodium nitrate, with 0.1 *N* silver nitrate, using the modified Müller electrode and the following electrode solution.

Ninety millilitres of 0.01 *N* potassium bromide solution, 6 ml. of 0.02 *N* silver nitrate and 6.0 g. of sodium nitrate (AnalaR) are mixed in a well-stoppered bottle. The bottle is well shaken and the precipitated silver bromide is allowed to settle. The clear supernatant liquor is then filtered through a fine filter-paper into a clean, dry bottle. The clean, dry capillary is then inserted in this solution, about 5 cm. of its length is filled, and the capillary is withdrawn. The outside of the capillary is rinsed with distilled water and the external electrode is placed in position.

In the titration of the reaction product of 25 ml. of a sample of bromine containing 0.006 per cent. by weight of chlorine with 25 ml. of 0.1 *N* potassium bromide solution, the end-points were quite precise at 25.67 and 27.00 ml. respectively of 0.1 *N* silver nitrate solution.

ORGANIC BROMINE COMPOUNDS

The following test has been found useful where the bromine is suspected to contain organic matter derived from bituminous constituents. Two grams of the bromine are dissolved in 30 ml. of 10 per cent. w/v sodium hydroxide solution and the solution is allowed to stand for 5 to 6 hours. The solution should remain clear and no oily drops should separate from it.

In a particular case of a badly contaminated sample of bromine we were able to isolate a white crystalline solid, which gave the following figures on analysis—

Carbon	3.98%
Hydrogen	Not detected
Chlorine	3.9%
Bromine	91.9%
Molecular weight	465

This apparently points to the presence of a carbon bromide containing a small proportion of chlorine. The presence of such bromides in commercial bromine is not unknown (Gmelin, Kraut²; Hermann,³ Poselger⁴ and Reymann⁵).

PRODUCTS OBTAINED BY THE ACTION OF BROMINE AND CHLORINE ON ALKALIES SUCH AS THE HYDROXIDES, CARBONATES AND BICARBONATES OF SODIUM, POTASSIUM AND CALCIUM

There are a very large number of possible combinations of the two halogens, bromine and chlorine, with various alkalies, but the general methods of analysis are much the same, particularly where the alkalies concerned are sodium and potassium hydroxides, carbonates, etc. Calcium compounds are dealt with similarly. The methods will be illustrated by reference to the various analytical tests which may be carried out on a preparation of the pure salts, potassium bromide, potassium bromate, sodium chloride, sodium chlorate and sodium carbonate, although it should be understood that these methods are of great flexibility and they may, with very slight modification, be adapted to a whole host of analytical problems. As a preliminary step it is desirable to dilute a known weight or volume of the preparation to a standard volume or weight.

TOTAL BROMINE AND CHLORINE—

An aliquot volume of the standard solution is treated with 15 ml. of a saturated solution of sulphur dioxide in water, then diluted to 100 ml. with distilled water and acidified with 5 ml. of 6 *N* sulphuric acid. The solution is boiled down to 50 ml. prior to determination of the total bromine and chlorine by Volhard titration.

TOTAL BROMINE CONTENT—

An aliquot volume of the standard solution is treated with 15 ml. of a saturated solution of sulphur dioxide in water. The solution is diluted to 100 ml. with water and acidified with 5 ml. of 6 *N* sulphuric acid. After boiling down to 50 ml., the solution is cooled, then neutralised to methyl red with *N* sodium hydroxide prior to the application of the Kolthoff and Yutzy method to the neutralised solution. The final titration is carried out with 0.1 *N* sodium thiosulphate solution.

Where the final titration is above about 12 ml. of 0.1 *N* sodium thiosulphate solution, it is always advisable to repeat the hypochlorite oxidation in the presence of 15 g. of added AnalaR sodium chloride in order to ensure efficient oxidation of the bromide to bromate. When the total chlorine and bromine are known and the bromine is determined as above, then the chlorine may be deduced by difference; this procedure will be sufficiently accurate for most purposes.

In certain cases, however, it may be desirable to check the amounts of bromine and chlorine by potentiometric titration after reduction to the halides. The procedure employed is illustrated by the following experiments, which were carried out on a solution prepared so as to contain—

2.9164 g. of potassium bromide	} in a total weight of 107.38 g. of solution.
0.7259 g. of potassium bromate	
0.4842 g. of sodium chloride	
0.4320 g. of potassium chlorate	
4.425 g. of sodium carbonate	
Distilled water	

The amount of the mixture required should give an approximate total potentiometric halide titration of 50 ml. of 0.1 *N* silver nitrate. A 2.1619-g. portion of the sample was diluted to about 50 ml., a large excess of a solution of sulphur dioxide in water (30 ml. of

0.3 *N*) was added, and this was followed by addition of 10 ml. of *N* sulphuric acid. After the solution had been boiled free of sulphur dioxide and cooled, it was titrated by the Volhard method, requiring 8.1 ml. of 0.1 *N* silver nitrate. From this result the amount of sample required to give a titration of approximately 50 ml. of 0.1 *N* total halide was calculated.

An 11.76-g. amount of sample was weighed out, diluted with distilled water, and 30 ml. of 0.3 *N* sulphurous acid solution and 23 ml. of *N* sulphuric acid were added, and the solution was boiled down to a volume of 50 ml. After addition of 2.5 g. of sodium nitrate (A.R.), the solution was submitted to potentiometric titration with 0.1 *N* silver nitrate by Clark's method.⁶

The titration units consisted of (a) a 250-ml. squat beaker, (b) a silver electrode consisting of a piece of No. 20 gauge fine silver wire which was sealed at the top into a short piece of glass tubing, which in turn fitted into a small rubber bung to serve as holder, (c) a calomel cell of the saturated potassium chloride type, prepared according to directions given by Clark⁷; the electrode vessel used was type G,⁸ (d) an ammonium nitrate bridge prepared according to Clark's directions,⁹ and (e) a stirrer, driven at about 200 r.p.m. by compressed air.

The potentiometer, by Muirhead & Co., Ltd., was capable of detecting differences of e.m.f. of the order of 0.0001 volt. The galvanometer was a Tinsley portable galvanometer having the following characteristics—

Resistance	325 ohms
Deflection per micro-amp.	10 mm.

Power was supplied by three Exide, 2-volt, 105 amp.-hr. storage batteries. A relatively new battery was used as a source of counter-e.m.f., and was always connected up to the potentiometer before the start of an experiment. Two 2-volt batteries were required to provide current for the galvanometer lamp.

In carrying out determinations by Clark's method it was found necessary to pay particular attention to the following points—

1. The silver-wire electrodes should be cleaned before each experiment. The wire electrodes were first polished with fine emery paper, then immersed in dilute nitric acid until gassing freely (it was found to be unnecessary to add nitrite) and finally washed well with distilled water.

2. During the course of the titration the electrode should be tapped lightly before each measurement of the e.m.f. is made in order to remove any silver halide which may have become attached to the electrode. If not removed in this way, the accumulation of silver halide round the electrode may lead to grossly inaccurate readings.

3. During the addition of silver nitrate solution it is desirable to interrupt the titration after the addition of every 5 ml. (or less) and wait for about 2 minutes in order to allow the system to attain equilibrium. The titration procedure is best illustrated by examination of the readings taken, each at 2-minute intervals, for the synthetic solution, given below (p. 377).

4. It is advisable to test the bridge frequently, preferably before each experiment, for contamination from the calomel cell, as even a minute amount of a saturated chloride solution would vitiate the results. To test the bridge, 50 ml. of distilled water are placed in the titration beaker, the bridge is inserted and the water is stirred, as in the actual determination, for 2 hours, after which time the water should still remain perfectly clear on the addition of a few drops of silver nitrate solution.

From the composition given on p. 375, the 11.76-g. sample contained—

0.3194 g. of potassium bromide	≡	26.83 ml. of 0.1 <i>N</i> halide
0.0795 g. of potassium bromate	≡	4.76 " "
0.05303 g. of sodium chloride	≡	9.07 " "
0.0473 g. of potassium chlorate	≡	3.86 " "

The results obtained were as follows—

	0.1 <i>N</i> halide	
	Added, ml.	Found, ml.
Bromine as (bromide + bromate)	31.59	31.67
Bromine as (bromide + bromate) + chlorine as (chloride + chlorate)	44.52	44.40

The e.m.f. and volume readings at the end-points were—

V, ml.	E, volts	$\frac{dE}{dV}$
31.49	0.0830	
31.61	0.0915	773
31.73	0.1017	977
31.85	0.1120	936
44.23	0.2522	
44.35	0.2828	2550
44.48	0.3272	3700
44.60	0.3475	1692

Although the above method of potentiometric titration may be applied to solutions containing bromide and chloride prepared by reduction of absorption liquors when the proportion of total chlorine to total bromine is comparatively high, it is not so suitable when the ratio of chlorine to bromine is low and the two potentiometric end-points lie close together.

It is then advisable, in the determination of small amounts of chlorine, to effect a preliminary separation of the bulk, but not all, of the bromine, before proceeding to the final potentiometric titration. Clark's method⁹ is suitable, and the manner of application is indicated by the method we have used to determine small amounts of chlorine in samples of sodium bromide.

For a particular sample of sodium bromide (B.D.H.), 2.5 g. of the sample were dissolved in about 200 ml. of distilled water, and 150 ml. of 6 *N* sulphuric acid were added, the solution was brought to the boil and 0.5 *N* potassium permanganate solution added dropwise to the boiling solution until a faint pink colour persisted; 47.0 ml. of 0.5 *N* permanganate were required. In the actual determination, a further 2.5 g. of the sample were treated as described except that only 44.6 ml. of 0.5 *N* permanganate were added dropwise. The solution was boiled free of bromine and the volume reduced to about 150 ml. After cooling the solution, 10 g. of sodium nitrate were added and the solution was titrated potentiometrically with 0.1 *N* silver nitrate by the method given on p. 376.

Good end-points were obtained in the application of the test to the sample of sodium bromide (B.D.H.) which contained 0.84 per cent. of sodium chloride, when the end-points were as follows—

V, ml.	E, volts	$\frac{dE}{dV}$
11.43	0.0970	1280
11.57	0.1153	2602
11.71	0.1525	1832
11.86	0.1787	
15.0	0.2580	
15.14	0.2806	1638
15.28	0.3258	4725
15.41	0.3580	2333

First end-point = 11.64 ml. of 0.1 *N* silver nitrate
 Second end-point = 15.22 ml. of 0.1 *N* silver nitrate

When the test was applied to known mixtures of potassium bromide and sodium chloride the following results were obtained—

Sodium chloride	
Added, %	Found, %
0.30	0.31
0.60	0.57
0.90	0.90

Although the potentiometric titrations were carried out with the equipment outlined above, it should be realised that comparable results would be obtained by using potentiometric titration devices on the market to-day, whether the balance point is obtained using a galvanometer or with the aid of a "magic eye."

CARBONATE CONTENT—

Into a 500-ml. Kjeldahl flask (see Fig. 5) of Pyrex or other hard glass, 50 ml. of concentrated hydrochloric acid solution, sp.gr. 1.10, is placed, together with 5 ml. of 0.5 *M* sodium arsenite solution and 5 ml. of ferrous sulphate solution (10 g. of ferrous sulphate (AnalaR) dissolved in 100 ml. of water). The flask is provided with a rubber bung through which passes a short, bent delivery tube of wide capillary tubing and a tap funnel C with a stem long enough to reach nearly to the bottom of the flask. A piece of rubber tubing is fitted over the stem at the point H where it is liable to touch the neck of the flask.

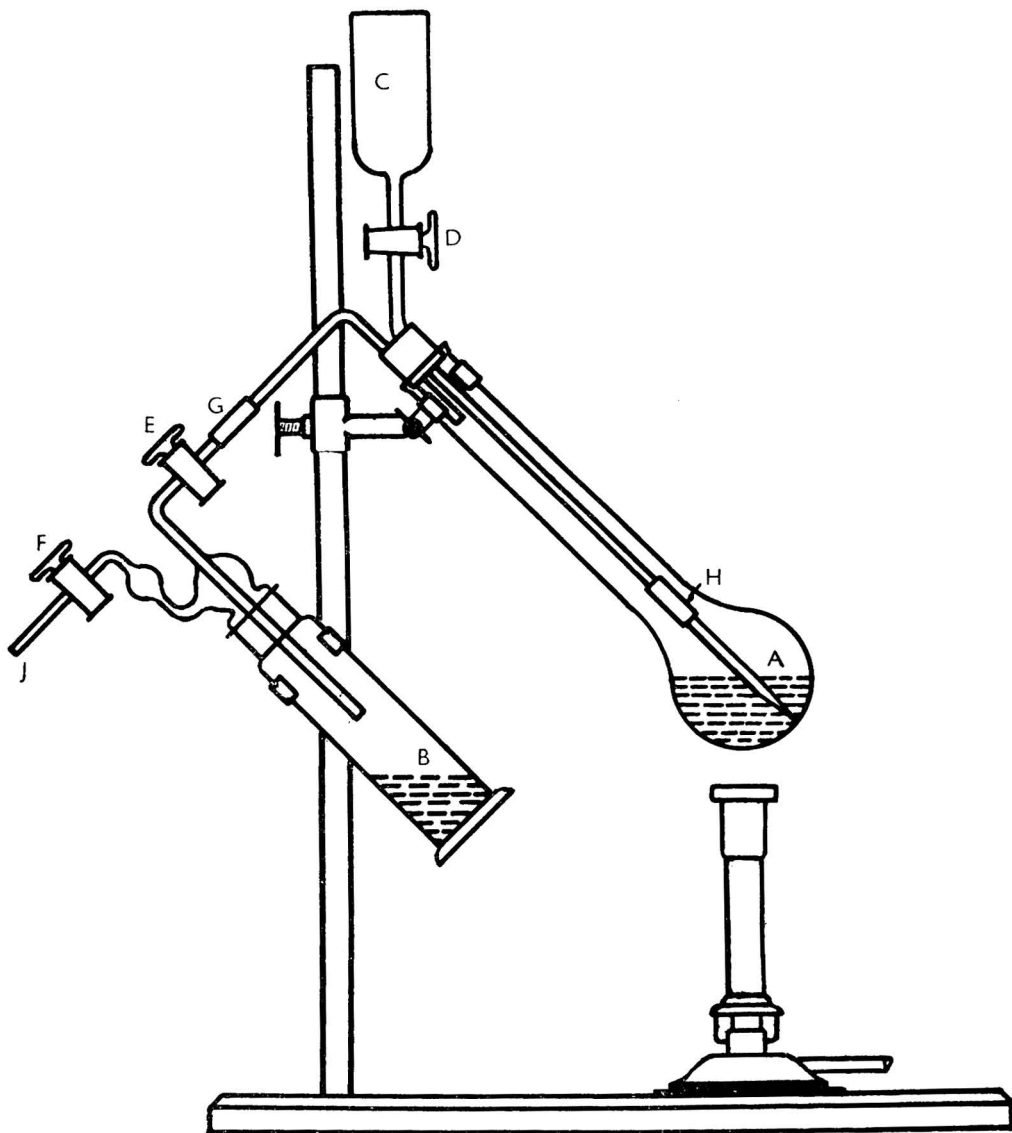


Fig. 5

Into a stout Drechsel bottle, B, provided with taps, are measured 20 ml. of carbonate-free *N* sodium hydroxide solution, 20 ml. of neutral 0.5 *M* barium chloride solution and 1 ml. of phenolphthalein solution (0.5 g. per litre of neutralised 50 per cent. v/v alcohol).

The Drechsel bottle is connected to the Kjeldahl flask and the whole is evacuated by means of a pump. The pressure after evacuation should not exceed 3 cm. of mercury. The solution of the appropriate amount of the sample under test is poured through the tap funnel into the flask, care being taken to avoid the admission of air, and then the tap funnel is closed with a rubber bung carrying a soda-lime tube. When only a few drops of solution remain in the tap funnel, the tap D is closed and the funnel rinsed several times with carbonate-free water, the rinsings going into the Kjeldahl flask. Weak hydrochloric acid is used for the last rinse.

Procedure—Mix the contents of the flask and add enough carbon dioxide-free water to bring the volume up to about 200 ml. Heat the flask over a small flame until the outlet tube becomes hot, shaking meanwhile. The solution in the Drechsel bottle should remain pink throughout the test. Admit air into the Drechsel bottle and disconnect it. Titrate the excess of sodium hydroxide with 0.5 *N* hydrochloric acid, using phenolphthalein as indicator. When the end-point, which should not be overstepped, is reached, add a few drops of screened methyl orange indicator and continue the titration to neutrality, using 0.5 *N* or 0.1 *N* acid according to the amount of barium carbonate precipitated.

If desired, excess of 0.5 *N* or 0.1 *N* hydrochloric acid may be added and the excess determined by titration with 0.5 *N* or 0.1 *N* sodium hydroxide solution. A blank test is carried out with the same quantities of reagents, but with the omission of the sample. The carbon dioxide content of the sample is deduced from the titration of the barium carbonate produced in the course of the test.

If the solution under examination contains such substances as bromides, bromates, chlorides and chlorates in addition to sodium carbonate, then the sodium carbonate may still, if required, be determined by direct titration. Similarly, the total alkali in a solution containing sodium hydroxide in addition to the above constituents may be determined. The method used involves titration with 0.1 *N* sulphuric acid. An aliquot of the solution, sufficient to give a final titration of about 30 ml. of 0.1 *N* sulphuric acid, is diluted to 100 ml., and 2 ml. of 0.1 *N* sodium thiosulphate solution is added prior to titration with 0.1 *N* sulphuric acid, using screened methyl orange as indicator. This device enables the end-point to be seen clearly without bleaching of the indicator.

MISCELLANEOUS DETERMINATIONS—

For some purposes it may be desirable to know the total halogen and the individual chlorine and bromine liberated on acidification of solutions of comparable type to that indicated on p. 375.

The total halogen rendered free is determined by the following procedure. An aliquot of the solution sufficient to give a final titration of approximately 40 ml. of 0.1 *N* sodium thiosulphate solution is treated with 5 ml. of 40 per cent. w/v potassium iodide solution and 25 ml. of 6 *N* sulphuric acid. The liberated iodine is titrated with 0.1 *N* sodium thiosulphate solution, with starch mucilage as indicator. The bromine rendered free is determined by the following procedure.

Direct method—An aliquot of the solution sufficient to give a final titration of about 20 ml. of 0.1 *N* sodium thiosulphate solution is transferred to the flask of an all-glass distillation apparatus, diluted to 100 ml. with distilled water, and 25 ml. of 6 *N* sulphuric acid is added from a funnel in the neck of the distillation flask. The tip of the all-glass condenser is immersed in a solution of 2.0 g. of sodium hydroxide (pellets from sodium) in 50 ml. of water to which 10 ml. of a saturated solution of sulphur dioxide in water has been added. The solution in the flask is boiled until colourless and until there is no visual evidence of halogen in the condenser. The time required for this operation is about 15 minutes. The condenser is rinsed out with a further 10 ml. of saturated sulphurous acid and then distilled water, and this solution is run into the condensate. The condensate and washings are collected and boiled down to 50 ml. in slightly acid solution, with methyl red as indicator. The acid solution is cooled, neutralised, and Kolthoff and Yutzy's method is applied.

Indirect method—A suitable aliquot of the solution is treated with 6 *N* sulphuric acid and the acid solution boiled until free from bromine. The residual acid solution is cooled and neutralised prior to application of the Kolthoff and Yutzy method. By this procedure the bromine not liberated by acid is obtained. This figure, when deducted from the figure for "total bromine" gives the bromine liberated by acid.

Incidentally, it has been shown that the principle of the method put forward by Pollard,¹⁰

i.e., vigorous aeration, is an excellent one for the rapid removal of bromine from aqueous acid solutions. The free bromine in 10 ml. of saturated bromine water is removed by this method in approximately $2\frac{1}{2}$ minutes.

The chlorine rendered free in this way is obtained by difference.

ACID SOLUTIONS CONTAINING HALOGENS—

These solutions rarely present much difficulty in their analysis. The degree of acidity may usually be determined by titration with standard alkali after removal of most of the free halogen by boiling and subsequent addition of 2 ml. of 0.1 *N* sodium thiosulphate solution prior to titration with standard alkali.

The free halogens may be determined by treatment with potassium iodide and titration of the liberated iodine with standard sodium thiosulphate solution, whilst the total bromine and total chlorine may be obtained after treatment of the acid sample solution with saturated sulphur dioxide solution, followed by boiling to remove sulphur dioxide and subsequent application of the methods outlined on p. 375.

DETERMINATION OF ALKALI METALS—

The determination of sodium and potassium in solutions similar to those indicated on p. 375 is effected by preliminary acidification with acetic acid of a known amount of the sample or sample solution followed by evaporation to dryness on the water-bath and subsequent determination of (1) sodium by the zinc uranyl acetate method, and (2) potassium by the cobaltinitrite - perchlorate procedure.¹¹

AMMONIUM CHLORIDE AND CALCIUM CHLORIDE—

Ammonium chloride—The direct determination of bromine by the modified method of Kolthoff and Yutzy was found to be inapplicable in the presence of ammonium chloride. This was proved by adding a known amount of potassium bromide (0.04 g. of potassium bromide, corresponds with a titration of 20.2 ml. of 0.1 *N* sodium thiosulphate) to 10 g. of ammonium chloride (AnalaR) and applying the modified Kolthoff and Yutzy's procedure to this solution. On the addition of the hypochlorite solution, a slight effervescence was noticed and the solution turned slightly yellow. The final titration obtained, *viz.*, 0.10 ml. of 0.01 *N* sodium thiosulphate proved conclusively that side reactions had inhibited the oxidation of bromide to bromate. This difficulty is overcome by boiling the solution with a slight excess of sodium carbonate until free of ammonia. The pH of the solution is then adjusted and Kolthoff and Yutzy's method applied. The actual method adopted is as follows—

Ten grams of ammonium chloride are dissolved in distilled water and treated with 11 g. of sodium carbonate (AnalaR). The solution is boiled until all the ammonia has been driven off and the volume has been reduced to about 50 ml. The solution is then neutralised to methyl red by the addition of 6 *N* sulphuric acid and the modified Kolthoff and Yutzy's method applied (*loc. cit.*).

A blank determination is carried out on 11 g. of sodium carbonate (AnalaR), the neutralisation being effected with sulphuric acid (hydrochloric acid was not used as it is liable to contain a relatively high proportion of bromine). The titration thus obtained is deducted from that obtained by oxidation of the sample.

Ammonium chloride (AnalaR) has been shown to contain 0.0009 per cent. of bromine and commercial samples of ammonium chloride about 0.005 per cent.

Calcium chloride—The calcium is removed by precipitation with sodium carbonate prior to oxidation with hypochlorite. About 10 g. of sample, accurately weighed in a stoppered weighing bottle, are dissolved in water. A solution of 11.0 g. of sodium carbonate (AnalaR) in about 50 ml. of water is then added and the mixture heated on a water-bath. After the precipitated carbonates have settled, the mixture is filtered and the precipitate washed well with hot water. The filtrate and washings are neutralised with 6 *N* sulphuric acid, using methyl red as indicator, and the volume is reduced to about 50 ml. by boiling. The modified Kolthoff and Yutzy procedure (*loc. cit.*) is then applied. The blank obtained on neutralising 11.0 g. of sodium carbonate (AnalaR) with 6 *N* sulphuric acid is deducted from the titration obtained in the determination.

AnalaR calcium chloride was shown to contain 0.001 per cent. of bromine and commercial calcium chloride about 0.03 per cent. of bromine.

ETHYLENE DIBROMIDE—

Organic substances such as ethylene dibromide may be examined by two methods.

1. *Total halogen*—About 0.3 g. of the sample accurately weighed in a small glass bulb with a sealed capillary end is fired in a Parr bomb with 15 g. of sodium peroxide, 1.5 g. of potassium nitrate and 0.5 g. of cane sugar in the ordinary way. The cold melt is extracted with water and a few ml. of saturated sulphur dioxide solution are added prior to acidification with 30 ml. of concentrated nitric acid and subsequent application of the Volhard reaction. The following result was obtained on a purified sample of ethylene dibromide, calculating all the halogen to the dibromide—

Ethylene dibromide added,	Ethylene dibromide found,
0.2944 g.	0.2940 g.

2. *Total bromine*—The reagents for this determination are those used in the ordinary modified Kolthoff and Yutzy method.

The decomposition of the sample is effected by sodium peroxide fusion in an electrically fired Parr bomb. The bomb charge consists of 0.25 g. of the sample, 1 g. of catalyst (potassium nitrate and dextrose in the ratio 2 to 1) and 13 to 14 g. of sodium peroxide. After firing and cooling, the melt in the bomb is leached out in a 500-ml. beaker containing about 100 ml. of boiling water. The solution is then boiled for 10 to 15 minutes. After cooling, the solution is made just acid with concentrated hydrochloric acid, re-cooled and diluted to 250 ml. in a volumetric flask. A 100-ml. aliquot is transferred to an 800-ml. beaker. It is neutralised to methyl red with *N* sodium hydroxide and then made just acid with *N* hydrochloric acid. Twenty-three grams of sodium chloride (AnalaR) and 4 g. of sodium hydrogen phosphate are now added, followed by 20 ml. of the hypochlorite reagent. The beaker is covered with a watch glass and the contents brought just to the boil over a bunsen flame. Then it is removed from the flame and 20 ml. of the sodium formate reagent are added to the hot solution.

The sides of the beaker and cover are carefully washed down and after standing for 5 minutes they are re-washed. The beaker is then cooled in a running water-bath. After cooling, 480 ml. of water are added, followed by 4 g. of potassium iodide, 100 ml. of 6 *N* sulphuric acid and 2 drops of the ammonium molybdate solution. The liberated iodine is now titrated with 0.1 *N* sodium thiosulphate, using starch as indicator.

DETERMINATION OF BROMINE IN THE ATMOSPHERE—

This determination does not correct for any traces of iodine in the atmosphere under test.

The reagents employed are those of the modified Kolthoff and Yutzy method (see Part I, p. 346). It is best to connect two absorbers in series and although considerable latitude is permitted in the choice of absorber it has been demonstrated that an impinger type based on the design given in Jacobs' "Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Vol. I, p. 81, Fig. 46, is very efficient for this type of work. Each absorber is charged with 23 ml. of 10 per cent. w/w potassium hydroxide solution (from pellets), and 100 litres of air are aspirated through the absorbers at the rate of 6 to 10 litres per minute.

The bromine in the individual absorbers is then determined by the following procedure and, with efficient absorption, the amount of bromine found in the second absorption vessel should be negligible.

Procedure—Measure 10.0 ml. of the absorber solution into a 250-ml. beaker, add 0.5 g. of sodium sulphite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$) and allow to dissolve. Now add 12.0 ml. of the 2.5 *N* hydrochloric acid solution, 25 ml. of water and 2 drops of methyl red indicator. Boil the solution down to a volume of 16 ml. (as indicated by a mark made previously on the beaker) in order to remove all traces of sulphur dioxide. Now add, from a burette, 10 per cent. potassium hydroxide solution until the solution is neutralised. In this neutral solution, dissolve 0.6 g. of sodium di-hydrogen phosphate and, after adding 3 ml. of the normal hypochlorite solution, insert a boiling rod, cover the beaker with a watch glass, and bring just to the boil. Remove from the source of heat, add 3 ml. of the sodium formate solution, gently blow away the vapours from the beaker and rinse down the sides of the beaker with about 10 ml. of water evenly spread over the surface area. After allowing the solution to stand for 10 minutes, again remove vapours and very carefully wash down with a further 10 ml. of water and cool thoroughly in cold running water. Now add 0.6 g. of potassium iodide, followed by 15 ml. of 6 *N* sulphuric acid and 1 drop of ammonium molybdate catalyst. Allow to stand for at least 1 minute and then dilute the solution to 90 ml. and titrate the

liberated iodine with freshly prepared 0.002 *N* sodium thiosulphate solution, with starch indicator.

1 ml. of 0.002 *N* sodium thiosulphate solution \equiv 0.02664 mg. of bromine.

Simultaneously with the test carry out a "blank" test on the reagents and distilled water. (With the reagents specified and the re-distilled water, the blank value should amount to the order of 0.02664 mg. only, *i.e.*, about 1 ml. of titrant.)

If *y* ml. = titration *minus* blank, then—

Concentration of bromine \equiv 0.02664 \times 23 \times *y* mg. per cubic metre.

URINE—

The method devised for the determination of bromine in urine is as follows. The figure obtained includes any small proportion of iodine in the samples.

The *N* sodium hypochlorite and sodium formate solutions are those normally prepared for the Kolthoff and Yutzy method (see Part I, p. 346).

Procedure—Place 5 ml. of 10 per cent. potassium hydroxide solution in a small nickel basin (2 inches in diameter) on a water-bath, add 50 ml. of the urine, 10 ml. at a time, and evaporate the mixture to dryness. Towards the end of the evaporation the contents of the basin must be mixed continually because of the formation of an incrustation on the surface of the mixture. Carry out this operation by holding the basin with a clean pair of crucible tongs and rotating it occasionally. Dry the evaporated residue in an air oven at 150° C. for 1 hour.

Ignite the dry solid in an electrically heated furnace set at a temperature of 480° C. Open the furnace door and allow the temperature to fall to 300° C., and then insert the nickel basin containing the dry solids. Close the furnace door and allow the temperature of the furnace to increase to 480° C. The complete ignition takes 1 hour.

Cool the ignited residue, add 10 ml. of re-distilled water, and heat the mixture on a water-bath for 5 minutes. Then filter the mixture through a 7-cm. Whatman No. 40 filter-paper, the filtrate being collected in a 250-ml. beaker. Wash the insoluble residue four times with re-distilled water, using about 5 ml. of water each time, and evaporate the filtrate and washings to dryness. Return the paper and insoluble matter to the nickel basin, add 1 ml. of 10 per cent. potassium hydroxide solution, and evaporate the mixture on the water-bath, and then dry at 150° C. for 1 hour. Ignite the paper and residue as before, *i.e.*, starting at 300° C. and raising the temperature to 480° C. for 1 hour.

Cool the ignited residue, add 5 ml. of dilute hydrochloric acid and stir the mixture well, then filter through a 7-cm. Whatman No. 40 filter-paper and collect the filtrate in the 250-ml. beaker containing the evaporated extract from the preliminary alkaline washing process. Then wash the insoluble residue twice with 5 ml. of re-distilled water for each washing, and collect the washings in the 250-ml. beaker.

Add 2 drops of methyl red indicator to the filtrate, and make it just acid by the cautious addition of dilute hydrochloric acid. Then neutralise the solution with 10 per cent. potassium hydroxide solution and dissolve 0.6 g. of sodium di-hydrogen phosphate in the neutral solution. Add 3 ml. of *N* sodium hypochlorite solution and cover the beaker with a small watch glass. Bring the solution just to the boil, then remove from the source of heat and add 3 ml. of sodium formate solution, and again rinse down the sides of the beaker with 5 ml. of water. When the solution has stood for 10 minutes, again wash down the beaker with 5 ml. of water, and cool thoroughly in running water.

Now add 0.6 g. of potassium iodide and follow by 15 ml. of 6 *N* sulphuric acid and 1 drop of ammonium molybdate catalyst. Dilute the solution to 90 ml. and titrate the liberated iodine with freshly prepared 0.002 *N* sodium thiosulphate solution, using 5 drops of starch solution, added near the end of the titration, as indicator.

1 ml. of 0.002 *N* sodium thiosulphate solution \equiv 0.0002664 g. of bromine.

Each test is corrected for a blank test on the reagents and the amount of re-distilled water used. This blank value was constant and amounted to 0.0002664 g.

The following results were obtained on application of the test to the urine of an analyst normally working in the analytical laboratory—

Added bromine,* g. per cubic metre	Bromine found, mg. per litre of urine
nil	3.25, 3.25
5	8.05, 8.25
10	12.8, 13.05

* Bromine added in the form of potassium bromide solution.

The method was now extended to the determination of bromine in snap samples of the urine of various members of the staff of the Research Laboratory; at the same time chloride tests were carried out by taking 5 ml. of the urine, adding 20 ml. water, filtering if necessary and washing the insoluble matter, then diluting to 100 ml. Excess of 0.1 *N* silver nitrate was added (10 ml.) and the mixture coagulated on a water-bath, then filtered off on a prepared asbestos Gooch pad, washed with water and dried at 100° C. as silver chloride. The following results were obtained—

	Bromine, mg. per litre of urine	Chlorine, mg. per litre of urine
Analytical chemist in Analytical Laboratory ..	3.25	3880
Chemist (Administrative)	7.06	5130
Chemist (Administrative)	4.1	5380
Clerk	2.9	3120
Chemist (mainly administrative)	5.41	11,740
Analytical chemist (engaged in metallurgical analysis involving considerable contact with bromine fumes)	6.22	10,070
Assistant chemist (ditto)	2.53	4390

I wish to take this opportunity of expressing my indebtedness to Mr. G. Moses, Mr. N. T. Wilkinson and the late Mr. J. Beeley for their assistance in these investigations.

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Part V. Apparatus for the Quantitative Estimation of Volatile Solutes

BY J. HASLAM AND A. T. WILLIAMSON

SYNOPSIS—Apparatus has been designed to prevent loss of bromine in the sampling and determination of this element in solutions containing it in the free state. The manipulation of this apparatus is described, and some characteristic results are given.

In the early stages of an experimental study of bromine equilibria, it was found that values for the concentration of the free halogen, obtained by the familiar iodide - thiosulphate method, were not reproducible. It was soon shown that the fluctuations were due to loss of bromine as vapour, and that special apparatus would be needed to avoid this loss.

It can easily be seen why this should be so. At 25° C., saturated bromine water has a partial bromine pressure of 213 mm.¹ and at the same temperature the total bromine in the liquid phase amounts to 0.215 moles per litre.² If we change the vapour-phase units we find that 213 mm. corresponds to 0.0115 moles per litre, *i.e.*, the vapour phase contains bromine at 0.0115/0.2141, or about 5 per cent. of its aqueous phase concentration. Violent agitation of bromine water with an equal volume of air will therefore cause a loss of nearly 5 per cent. of the liquid-phase bromine; with less extreme treatment the loss may be smaller, but it should never be overlooked. Such an apparently innocuous procedure as sucking a bromine water sample into a pipette may lead to appreciable errors from this cause, and the effect

should be expected whenever a solute is so volatile that its concentration in the gas phase is appreciable with respect to its concentration in the liquid phase.

THE EXPERIMENTAL SOLUTION

Samples of bromine water and brominated brines have been taken from the reaction vessel, which is a Jones "Equilibrator,"³ by means of the technique adopted by Jones and

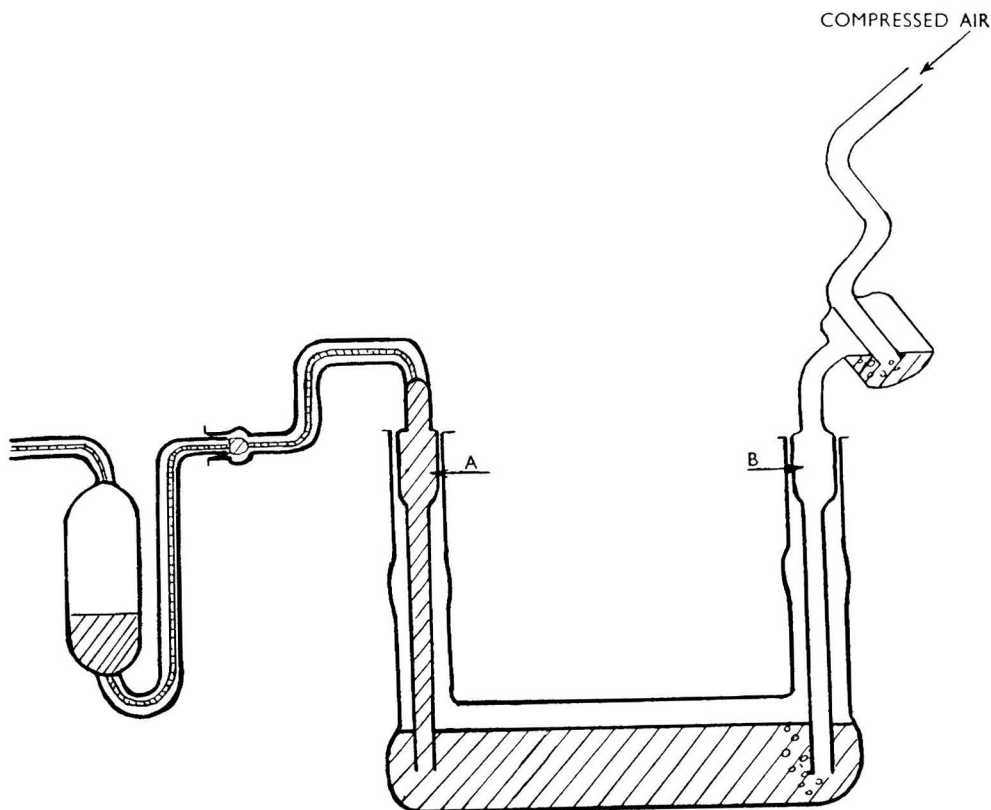


Fig. 1. Schematic diagram showing the experimental arrangement for filling the pycnometer

Baekstron.³ This method is made clear by a schematic diagram (Fig. 1). At the end of a run, ground stoppers are removed from A and B, and are replaced by a delivery tube and a pre-saturator. A pycnometer is attached to the former, the pre-saturator is filled with liquid by tilting the apparatus, and a very slow stream of compressed air is passed into the reaction vessel. The liquor sample is forced into the pycnometer, and the displaced liquid is replaced by air which has been given nearly the correct bromine content by the pre-saturator.

The first portions of the sampled liquor lose bromine vapour inside the pycnometer, and must be discarded. This is done simply by continuing the passage of liquor until the weak portions have been flushed through the pycnometer. It has been found that the expulsion of about 20 ml. of liquor after filling a 50-ml. pycnometer completely eliminates the dilute portions, and the density values for a given solution, *e.g.*, saturated bromine water, have been reproducible within 0.0001 units.

When the pycnometer has been correctly filled, the compressed air supply is cut off, a ground-glass cap is placed over the exposed pycnometer arm, and the other arm is disconnected from the reaction vessel delivery tube. A second glass cap is put over the end of this freshly exposed arm, and the sample is ready for weighing.

To determine the total free halogen, the weighed pycnometer is turned upside down,

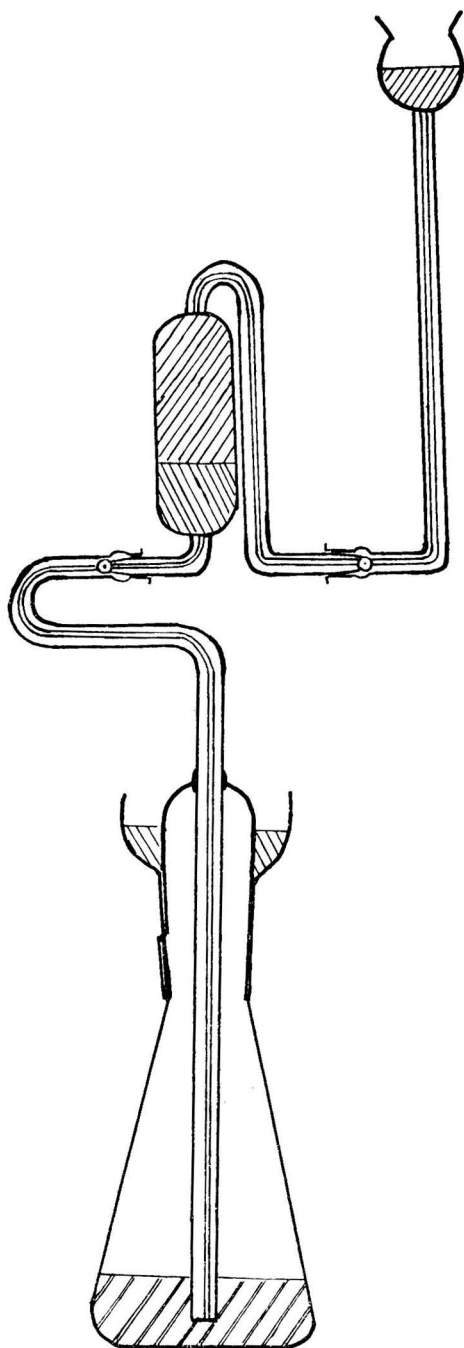


Fig. 2. Apparatus for discharging the contents of the pycnometer into potassium iodide solution

its caps are removed, and it is connected to the apparatus shown in Fig. 2. This consists of a flask which was originally designed by one of the authors (J. H.) for the determination of phenols by the bromide - bromate - acid method, and which has been modified by the addition of a special inlet tube to facilitate direct connection with any one of a number of pyknometers by means of a ground-glass joint with a standard taper.

The flask holds an excess of potassium iodide solution that covers the lower end of the inlet tube. Its ground stopper is so rotated that a small quantity of potassium iodide solution can be placed in the annular trap above the joint without leaking into the flask below, yet air can escape from below to the atmosphere by percolating through the liquid in the trap.

One end of the pyknometer is attached to the inlet tube, the other is provided with a thistle funnel. By pouring a small portion of distilled water into this funnel, displacement of the sample liquor is begun. As it drains into the flask, the thistle funnel is constantly replenished with wash-water, which forms a sharp boundary with the bromine water by virtue of its lower density and the absence of turbulence. The sharpness is particularly marked if a small bubble of air is sucked into the pyknometer shortly after movement has begun. This seems to act by forcing the incoming wash-water to enter in a slow stream shaped like a hollow cone with the bubble in the hollow. Without the bubble the water would enter in a narrow pencil-like stream with a high velocity, and would cause a certain amount of mixing of the two layers.

When practically all the sample has been displaced by wash-water, a small portion of potassium iodide solution is added to the thistle funnel to remove the last traces of bromine. This iodide solution, being denser than water, causes violent convection in the pyknometer and scours it effectively. It is followed by final doses of wash-water, which float on top of the denser iodide layer, and which show up clearly above the pale yellow iodide - iodine mixture. This final portion of wash-water is allowed to drain into the flask.

Meanwhile, the bromine water entering the flask has been reacting with the excess potassium iodide in the flask itself, and displacing air through the guard solution of potassium iodide in the annular space above the stopper. When the process is complete, the thistle tube and pyknometer are removed, the guard solution is allowed to drain into the flask by rotating the ground stopper, and this stopper itself is removed and washed with a spray of distilled water, the washings running into the flask. The sample is then titrated in the usual way with standard sodium thiosulphate solution.

This procedure has given the greatest satisfaction. From start to finish the sample is guarded against loss of volatile matter, and is exposed to the air only after it has been allowed to react completely with the excess of potassium iodide. Titrations on solutions of the same composition, *e.g.*, pure saturated bromine waters, have been consistently reproduced within 1 part in 1000; and separate experiments on the guard solution of potassium iodide have shown that the amount of free halogen that reaches it is completely negligible.

A great deal of the credit for the satisfactory solution of this problem must be given to J. Welbergen, whose skilful fabrication of all the glassware, including the vitally important interchangeable ground-glass joints, provided us with the desired apparatus. We are also indebted to C. Lynch for assistance in the experimental investigations.

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DISCUSSION ON THE ABOVE FIVE PAPERS

Mr. W. M. SEABER said that he had listened to the papers with very great interest. He thanked Mr. Haslam for his kind references to his early work on the fluorescein method. He had never regarded this method as being more than roughly quantitative, and he had applied it only in connection with the examination of goods suspected of having suffered damage from sea-water. He had found it of some use in that respect, although he recognised that there were difficulties to be overcome in its working.

He would be very interested to try Mr. Haslam's method.

Mr. R. C. CHIRNSIDE said he would like to congratulate Mr. Haslam and his fellow authors, not only on the excellent analytical work which they had described, but also on the method of presentation of the whole subject. The significance and importance of reliable analytical work in the development of industrial processes had been very clearly demonstrated.

Dr. J. H. HAMENCE congratulated the authors on their papers and on the attractive manner in which they had been presented. He stated that he had had an opportunity of trying out in the laboratory the method put forward by the authors for the estimation of small amounts of bromine. The method was found to be a very good one, and to give excellent results. He had also found the method of considerable value for the estimation of small amounts of bromine in commodities alleged to have been damaged by sea-water.

There was one point, however, in connection with the application of the method for sea-water damage which he thought should be emphasised. The majority of substances which were examined for sea-water damage were natural substances of an organic nature, and before the bromine test was applied, it was necessary to destroy the organic matter, usually by ignition with an alkaline substance such as sodium carbonate or lime.

A number of experiments had showed that before employing the method described by the authors to the ashed material, it was of the utmost importance to ensure that the whole of the organic matter was destroyed. If traces of organic matter were allowed to remain, these sometimes absorbed chlorine on treatment with sodium hypochlorite, and this absorbed chlorine frequently reacted in the last stages of the operation with the potassium iodide, thereby giving rise to erroneous results.

Dr. Hamence also suggested that the method described for the preparation of the sodium formate solution should be modified, as with the directions at present given in the paper, an almost explosive reaction resulted when the formic acid and the caustic soda were mixed. Dilution of the formic acid with a little water before starting the preparation avoided this trouble.

He also asked the authors if they could explain the use of the 1 drop of ammonium molybdate in the reaction.

Mr. N. T. WILKINSON congratulated all the authors on the presentation of the papers and asked whether it was essential to have both ferrous sulphate and sodium arsenite to absorb bromine liberated in the determination of carbon dioxide.

Mr. HASLAM agreed with Dr. Hamence's observations about the need for prior removal of organic matter before application of the hypochlorite oxidation method. The authors had always taken particular precautions about this, as could be seen in the method which they had used for the determination of bromine in urine.

With regard to the second point about the preparation of sodium formate solution, it should be realised that the addition of formic acid to sodium hydroxide solution could only be carried out with care and attention. During the war they had prepared very large volumes of this reagent as a matter of day-to-day routine. The sodium hydroxide solution, prepared by solution of the pellets in a small volume of water, was contained in a large beaker surrounded by ice mixture, and the formic acid was led in from a separating funnel provided with a bent delivery tube with the delivery end against the side of the beaker. The sodium hydroxide solution was stirred mechanically during the initial dropwise addition of the formic acid. After the preliminary reaction the remaining formic acid could be added more quickly.

In connection with the point about the molybdate, it had always been suggested¹ that the excess formate introduced in the removal of the excess hypochlorite slowed down the reaction between bromic acid and hydriodic acid, and the purpose of the molybdate was to catalyse this latter reaction and overcome the influence of the formate.

With regard to the point raised by Mr. Wilkinson, Mr. Haslam indicated that it was quite probable that one of the reagents alone, *i.e.*, either sodium arsenite or ferrous sulphate, would be sufficient to prevent the interference of bromine in the carbon dioxide determination. He had not carried out extensive experiments to test the point and had rather "played for safety" in keeping to both substances.

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A Modified 2:4-Xylenol Method for Nitrate Estimations

By H. BARNES

SYNOPSIS—The difficulties of the phenol disulphonic acid method are briefly considered together with the advantages of the 2 : 4-xylenol technique. A method is outlined whereby the distillation in the 2 : 4-xylenol method is replaced by a double extraction technique. The method is flexible and can be adapted to the determination of very small quantities of nitrate, less than 2 μ g. per 5 ml. The double extraction enables some colour due to organic materials to be eliminated; larger amounts can be allowed for by blank determinations, but the results are less reliable. Evidence is presented that the method is much more tolerant to the presence of chlorides than the disulphonic acid technique.

A SURVEY of the extensive literature on the estimation of nitrates by means of phenol-disulphonic acid indicates that with adequate precautions and with the use of a pure disulphonic acid reagent^{1,2,3,4} nitrates can be accurately estimated in aqueous solutions even when some other salts are present in moderate quantities. Difficulties arise, however, when solutions containing organic matter or chlorides are to be investigated.

The difficulties with solutions containing organic matter are due to the following causes.

(1) The colour, if not removed, interferes with the colour of the yellow nitration product obtained on making the solution alkaline.

(2) If agents are used to remove the colour they may absorb nitrates.

(3) Even after removal of colouring matter, organic material may still be left in solution; this may char on addition of the reagent, and reduction of nitrate may also take place at this stage.

The use of 2 : 4-xylenol, as described by Blom and Treschow,⁵ minimises some of these causes of error, and also renders unnecessary some of the precautions which need to be taken with the standard phenol reagent. The xylenol method does not require evaporation of the solution to dryness, and precautions against loss of material due to acidity during evaporation, and against mechanical losses on adding the reagent to the dry residue, are unnecessary. Furthermore, the precipitation of heavy metals on making alkaline is avoided.

As the acid mixture used is only 70 per cent. (by volume) and the nitration product is distilled off from the mixture, coloured products will not interfere except by reduction of nitrate in the heating (nitration) stage, and, with the reduced acid concentration, errors from this source will tend to be less than those with the standard phenoldisulphonic acid reagent. Further, the lower acid concentration would be expected to lessen the error caused by chlorides.

The 2 : 4-xylenol method would, therefore, appear to have considerable advantages, and its relative neglect in comparison with the phenoldisulphonic acid method is perhaps due to the time and apparatus involved in the distillation process. It is the object of the present paper to describe a modified form of the method which avoids the distillation.

In view of the fact that Blom and Treschow's⁵ paper is somewhat difficult of access, however, it may first be useful to summarise their procedure and results. Two ml. of the nitrate solution were treated with 50 ml. of 55 to 70 per cent. (by volume) sulphuric acid. After heating for $\frac{1}{4}$ hour at 30° C., 0.1 ml. of 2 : 4-xylenol was added and the mixture was shaken and then heated at 30° C. for a further 1 to 2 hours with the flask stoppered. After cooling, 150 ml. of water were added, the solution was transferred to a distillation apparatus fitted with a trap, and 75 ml. were distilled over into 25 ml. of 0.2 *N* sodium hydroxide contained in a graduated flask cooled in water. After the solution in the receiving flask had been cooled to room temperature, the colour developed was compared either with that from a known quantity of nitrate similarly treated or a pure solution of nitro-*m*-xylenol in alkali. In the latter case a correction factor was applied to allow for the fact that nitration is not 100 per cent. efficient.

Blom and Treschow noted that—

(1) The speed of nitration with a given acid concentration depends upon the temperature; 7 hours were required at 18° C., whereas at 30° C. the reaction was complete in $\frac{1}{2}$ hour.

- (2) At 30° C., the acid concentration could be varied from 55 to 70 per cent. (by volume) without affecting the nitration.
- (3) The yield of nitro-xyleneol was about 73 per cent. of the theoretical value.
- (4) A 12-fold to 15-fold excess of xyleneol over nitrate was required; further increases in xyleneol added did not influence the nitration yield.
- (5) 98 per cent. of the nitro-xyleneol distilled over in the first 25 ml. of distillate.
- (6) Wide variation in the alkali concentration in the distillate did not affect the colour development.
- (7) For colour comparison the solutions should be at the same temperature, as the intensity increased 0.62 per cent. per degree rise in temperature.
- (8) Oxidising agents should be absent, as they tended to oxidise xyleneol to a coloured complex which passed into the distillate.

A MODIFIED 2 : 4-XYLENOL TECHNIQUE

The method described below obviates the distillation by utilising the fact that the nitro-xyleneol is readily soluble in organic solvents, from which it can be extracted by sodium hydroxide solutions.

METHOD

REAGENTS AND APPARATUS—

- 2 : 4-Xyleneol (B.D.H.): 1 per cent. solution in acetic acid.
- Sulphuric acid (nitrogen-free): 85 per cent. by weight in water.
- Sodium hydroxide (A.R.) solution: 0.4 *N*.
- Toluene (A.R.).
- Separating funnels.

The transmittances were determined on a Spekker absorptiometer, using violet filters (Ilford No. 601) and the cells appropriate to the particular amount of extract obtained.

For micro-quantities a special separating funnel with a double cock described below was used.

PROCEDURE—

Take 5 ml. of nitrate solution and add 15 ml. of the acid. Allow to cool and add exactly 1 ml. of the xyleneol reagent. Heat in a water-bath for $\frac{1}{2}$ hour at 35° C. Heating should be done in stoppered tubes. Cool, add 80 ml. of water, cool again and transfer to a separating funnel. Add 10 ml. of toluene and shake thoroughly but not too vigorously for a few minutes, avoiding emulsification. Allow to stand for 15 minutes and then run off the lower layer. Add 10 ml. of the 0.4 *N* sodium hydroxide solution and shake gently for 5 minutes. Allow to stand until clear. Transfer the required quantity of the lower layer to a 1-cm. Spekker cell and measure the transmittance, using violet filters and setting the instrument against pure water.

A calibration curve is constructed using known quantities of nitrate and a blank should be run, to allow for impurities in the reagents and for the extraction of the unchanged xyleneol. The temperature of the solutions used in calibrating should be noted.

NOTES ON THE METHOD

(1) The nitro-xyleneol can be extracted by numerous organic solvents. Toluene is convenient because it is very insoluble in water, and as upper layer it can be left in the funnel after shaking with the nitrated mixture; a heavy solvent would have to be transferred to a second funnel for shaking with caustic soda.

(2) An extra washing of the toluene solution, subsequent to extraction of the nitro-xyleneol may be introduced if desired. This helps to wash out the bore of the stopcock.

(3) The shaking should be thorough but not too vigorous. The toluene - caustic soda mixture shows a distinct tendency to emulsify and matters should be arranged for it to stand until quite clear, if necessary, for an hour.

(4) Between 0 and 21 μg . of nitrate nitrogen per 5 ml. a linear calibration curve is obtained; 1.0 μg . of nitrate nitrogen corresponds to a drum difference of 0.025, so the sensitivity is of the order of 0.1 μg .

(5) If the amounts of xylenol suggested in the original work are used, a very high blank is obtained due to the extraction of the unchanged xylenol. It was shown that the amount recommended above is adequate for maximal nitration. In view of subsequent work with smaller quantities, considerable attention was given to the blank determination and it was shown that it could be entirely accounted for by the acid - water mixture, toluene and xylenol reagent. Confidence in the constancy of the blank is necessary before the method can be used for the smaller quantities of nitrate. For the lower ranges of nitrate smaller quantities of reagent can be used, with a reduction in the blank.

(6) The following are typical results obtained by the method.

TABLE I

Nitrate nitrogen, $\mu\text{g.}$ per 5 ml.

Present	4.2	5.3	8.4	10.5	12.6	16.8	18.9	21.0
Found	4.5	5.5	8.4	10.4	12.7	17.1	18.3	21.7

(7) The double extraction, toluene and caustic soda, enables a considerable amount of organic matter to be eliminated; much of it is frequently insoluble in toluene in the first extraction and such as is soluble tends to be retained when shaking with alkali. It was found that, by carrying through a blank on the test solution without the addition of the xylenol reagent, allowance could be made for the colour due to comparatively large quantities of organic matter, although the blank was then very high. In these circumstances, however, the results were somewhat less accurate than in the absence of organic matter as is indicated in Table II. In these experiments sucrose was added and allowed to char during the nitration.

TABLE II

In all the tests 10.5 $\mu\text{g.}$ of nitrate nitrogen were present per 5 ml.

Sucrose present, mg./5 ml.	Nitrate nitrogen found, $\mu\text{g.}/5$ ml.
5	9.5
10	10.7
20	9.3

The effect of these large quantities of organic matter on the blank is considerable.

(8) The method is to some extent flexible since the proportions of nitrate solution and acid mixture can be varied if the final concentrations are maintained as given above. By this means evaporation of the sample can often be avoided. By reducing the amount of toluene and caustic soda or by increasing the amount of nitrate solution the sensitivity of the method can be greatly increased.

(9) Amounts of nitrate nitrogen less than 2 $\mu\text{g.}$ per ml. can be dealt with as follows: 1 ml. of the test solution, 3 ml. of the acid and 0.1 ml. of a 0.1 per cent. xylenol solution are treated as described under Procedure. After cooling add 5 ml. of distilled water. After again cooling, shake with 1 ml. of toluene, separate, and wash the toluene extract with 1 ml. of water. Add 1 ml. of 0.04 N sodium hydroxide, shake, separate and measure transmittances using a 1-cm. micro-cell, capacity 0.6 ml. If separation is difficult the yellow extract can be centrifuged.

In these circumstances 1 $\mu\text{g.}$ corresponds to 0.250 drum divisions, so that the sensitivity is of the order of 0.01 to 0.02 $\mu\text{g.}$ For such small quantities the blank is comparatively high, amounting to an equivalent of 0.06 $\mu\text{g.}$ but it is constant. By this method the following results were obtained and are typical of the technique.

TABLE III

Nitrate nitrogen, $\mu\text{g.}$ per ml.

Present	0.84	0.42	0.21	0.10
Found	0.86	0.41	0.23	0.09

For these small amounts a special funnel was used. A two-way cock was fused into a small separating funnel, the two outlets being of small bore tubing. In this way the extracted nitration solution could be run off without contaminating the tube through which the caustic soda extract was run off.

(10) In view of the lower concentration of acid employed it would appear possible that the method could be applied in the presence of larger amounts of chloride than is permissible in the disulphonic acid method.

With the above technique (5 ml. of solution and extracting with 10 ml. of toluene) the following results were obtained on addition of sodium chloride to the nitrate solution.

TABLE IV

EFFECT OF CHLORIDE

NaCl added, mg./5 ml.	0	0.14	0.28	0.56	1.13	2.26
Nitrate nitrogen found, $\mu\text{g.}/5$ ml.	5.3	5.3	5.3	4.3	4.0	3.3
	10.5	10.2	9.5	6.8	—	—
	21.0	21.0	20.1	18.2	—	—

It would appear that small amounts of chloride may be present without serious interference with the estimation of quantities of nitrate of this order; and the method is more tolerant of chlorides than is suggested for the disulphonic acid technique.

(11) An interference is caused by the presence of nitrites, and these must be oxidised and determined as nitrates, allowance being made by a separate determination of nitrite. Since in water analysis nitrites are usually determined separately, this involves little additional work. As noted previously, precaution should be taken to ensure complete destruction of any excess oxidising agent present.

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MARINE STATION

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October, 1949

Notes

USE OF OXALIC ACID IN THE DETERMINATION OF ASCORBIC ACID

In the determination of ascorbic acid by titration with 2 : 6-dichlorophenolindophenol, metaphosphoric or oxalic acid is used (a) as a stabiliser for ascorbic acid¹ and (b) in the standardisation of the dye with ferrous salts.² The presence of metaphosphoric or oxalic acid is necessary for the reaction of ferrous ions with the dye. Solutions of metaphosphoric acid are comparatively unstable and oxalic acid is sometimes preferred. The effect of light on solutions of oxalic acid, however, has not been sufficiently emphasised.

In the titration of ferrous ammonium sulphate with the dye, solutions of 2 per cent. oxalic acid which had been kept for a day or more in ordinary glass bottles were found to give a low titre. In the extreme case of solutions kept near a well lighted window for 7 days, the titre was less than one-fifth of that obtained with fresh solutions (or solutions protected from light), e.g., 2 ml. of a 0.1 per cent. solution of ferrous ammonium sulphate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 0.1 N sulphuric acid were mixed with 10 ml. of a 2 per cent. solution of oxalic acid ($(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) and titrated immediately.

Oxalic acid solution	0.001 N dye, ml.
Freshly prepared	5.1
Kept near window for 7 days	0.1-0.6

The loss of oxalic acid from solution under the influence of light was reported by Ishimaru,³ but this loss is comparatively slow and in the experiments just quoted was only 1 to 2 per cent. of the original concentration. The interference is more probably due to traces of hydrogen peroxide, which Dain and Kutsaya⁴ have shown to be a product of the photochemical oxidation of oxalates. This is indicated by the following test.

Five millilitres of a 2 per cent. solution of oxalic acid ($(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$) were mixed with 0.25 ml. of 10 per cent. solution of potassium iodide and 0.25 ml. of 1 per cent. starch solution.

The fresh oxalic acid solution gave no colour, while the solution exposed near a window for 7 days developed an intense blue colour immediately after adding the reagents.

It is suggested that the peroxide in the deteriorated oxalic acid solution rapidly oxidises the ferrous ions and causes a low titre. Although deteriorated oxalic acid solutions failed to promote appreciable destruction of pure ascorbic acid, such destruction cannot be excluded in view of the possibility of catalysts in extracts of natural products.

For use in the titration of ferrous iron, it has been found necessary to keep solutions of oxalic acid in dark bottles wrapped in black photographic paper. Solutions so kept have been found quite satisfactory for this purpose after six months.

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DIVISION OF FOOD PRESERVATION
COMMONWEALTH SCIENTIFIC AND
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F. E. HUELIN
December, 1949

DETERMINATION OF RARE EARTHS

SINCE the publication of the Spectrographic Determination of Rare Earths using the Intermittent Arc Technique,¹ further work has shown that the use of copper as a supporting electrode in the place of graphite gives definite advantages. Simpler operating conditions and spectra relatively free from interfering background are obtained at the cost of a slight loss in the lowest limits of sensitivity.

Electrodes of hard-drawn copper about 1 inch in length and $\frac{1}{4}$ inch in diameter were used; the preparation of the electrode surfaces and coating thereof was carried out in exactly the same manner as with graphite electrodes.

The loss in the lowest limit of detectability is slight but would amount approximately, *e.g.*, for yttrium, to a change from 0.0005 to 0.001 per cent. Except in special cases, this is fully offset by advantages gained in other respects.

The advantages gained by the use of copper electrodes are—

1. Copper is readily obtained in a pure form and unlike graphite, does not vary appreciably with its origin, and so affect the determination of rare earths.
2. The interference caused by the band spectrum of the graphite arc in the presence of atmospheric nitrogen does not arise; therefore not only are variations in the general background, due to the bands, overcome, but also rare earth lines may be used which occur in the region of the spectrum where interference would otherwise exist. By making use of a wider choice of lines it should be possible in some instances to compensate for the reduction in sensitivity.
3. The consumption of electrode material is very much reduced, as copper electrodes are easily cleaned and used again.

Adequate sensitivity has been obtained for several of the elements by using the lines listed in the original paper on the subject. Further work is in process to establish the most suitable line pairs and any improvement in reproducibility brought about by this technique.

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J. A. C. MCCLELLAND
February, 1950

Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1950, **75**, 283).

<i>Public Analyst</i>	<i>Appointments</i>
CAHILL, Terence John (Deputy) ..	County of Westmorland.
CAHILL, Terence John (Deputy) ..	County Borough of Darlington.
CHAPMAN, William Bernard (Deputy) ..	County Borough of Portsmouth.
CHAPMAN, William Bernard (Deputy) ..	County of Isle of Wight.
RYMER, Thomas Edward (Deputy) ..	County of Surrey.
WILLIAMS, Albert Lester	County of Isle of Wight.

OFFICIAL AGRICULTURAL ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1950, **75**, 111).

<i>Agricultural Analyst</i>	<i>Appointments</i>
ALLEN, David George (Deputy) ..	County Borough of Northampton.
CAHILL, Terence John (Deputy) ..	County of Westmorland.
CAHILL, Terence John (Deputy) ..	County Borough of Darlington.

British Standards Institution

NEW SPECIFICATIONS*

British Standards for Solvents and Allied Products—

- B.S. 506 : 1950. Methyl alcohol (Methanol).
- B.S. 507 : 1950. Ethyl alcohol (Ethanol).
- B.S. 508 : 1950. Normal butyl alcohol (Butanol).
- B.S. 509 : 1950. Acetone.
- B.S. 549 : 1950. Diacetone alcohol.
- B.S. 551 : 1950. Normal butyl acetate.
- B.S. 552 : 1950. Amyl acetate.
- B.S. 553 : 1950. Ethyl acetate.
- B.S. 573 : 1950. Dibutyl phthalate.
- B.S. 574 : 1950. Diethyl phthalate.
- B.S. 575 : 1950. Carbon tetrachloride.
- B.S. 576 : 1950. Acetic acid.
- B.S. 580 : 1950. Trichlorethylene (Types A, B and C).
- B.S. 662 : 1950. Carbon disulphide.
- B.S. 663 : 1950. Ethyl lactate.
- B.S. 1593 : 1950. Perchloroethylene.
- B.S. 1594 : 1950. Diacetin (Glyceryl diacetate).
- B.S. 1595 : 1950. *iso*Propyl alcohol (*iso*Propanol).

Price 2s. each, post free, except B.S. 576, which is 2s. 6d.

The British Standards Institution has just issued the Standards listed above as the first eighteen in a new series for solvents and allied products. Most of them are revisions of those published between 1933 and 1936, but the last three are completely new. The requirements and methods of test in these standards have been brought up to date as recommended by manufacturers and users. The publication of other standards in the series will follow shortly, including several for important materials used as plasticisers.

B.S. 684 : 1950. Methods of analysis of oils and fats. Price 7s. 6d.

* Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

Reviews

CHEMISTRY OF SPECIFIC, SELECTIVE AND SENSITIVE REACTIONS. By FRITZ FEIGL. Translated by R. E. OESPER. Pp. xiv + 739. New York: Academic Press Inc. 1949. Price \$13.50.

Every member of the Society of Public Analysts must know of Professor Feigl's extensive work in developing spot tests for most inorganic ions and for many organic groups and molecules. He is so obviously the authority on the subject that a book upon it by him is assured an appreciative reception. Feigl's "*Qualitative Analyse mit Hilfe von Tüpfelreaktionen*" (Leipzig, 1930) has become available in English in two parts. The practical section was translated by Dr. Janet Matthews and published in 1937; later editions have been Dr. Oesper's translations. The theoretical part of the German text was not published in English until 1940, when the Elsevier Publishing Co. Inc. of New York released "Specific and Special Reactions for Use in Qualitative Analysis, with Particular Reference to Spot Test Analysis"; this 192-page book was another of Oesper's translations. The theoretical work has now been completely revised and considerably expanded; it is described under the new title, "Chemistry of Specific, Selective and Sensitive Reactions." In the preface we are told that "the author began his preparatory studies long before the war, but the laboriously gathered material was lost during his flight from Europe": we sympathise with him for his unpleasant experiences and we admire his tenacity of purpose from which we benefit so much.

The new title is apt and the omission of any limitations to spot tests or to qualitative analysis is significant, although many of the practical consequences of the theoretical considerations have been qualitative microchemical tests. The book is concerned with the chemistry—inorganic, organic and physical—of numerous reactions and it cannot be over-emphasised that, as such, it is of the greatest interest and importance to all chemists; it is most unusual for a member of the profession to escape analysis completely, but even such a *rava avis* would find many parts of the book useful. The author says he has three groups of readers in mind: those "who wish to know the chemical basis of many modern analytical procedures," those actively engaged in research in analytical chemistry, and those interested in "experimental chemistry as a part of science which is still a fertile field for the trained and alert investigator." All three types will undoubtedly benefit from Feigl's industry in writing this comprehensive book for them.

There are so many experimental facts, derived from all branches of chemistry, that it is impossible to report them in a review, and it is difficult even to give an adequate synopsis. After a brief consideration of the requirements for a chemical reaction which is to find analytical application, a full description is given of the meanings attached to "specific," "selective" and "sensitive" in the title. All who write about qualitative tests should be encouraged to use these terms precisely, and their attention should be drawn to the "region of uncertain reaction," so named by Emich; much misunderstanding might then be avoided. The third chapter is also fundamental in character; it is a review of the various types of co-ordination compounds. These find repeated application throughout the book and are the commonest means of masking an undesired reaction. The reactivity of a substance may also be *enhanced* by the formation of a complex: this feature is discussed in a chapter on catalysed and induced reactions and on induced precipitation and solution of compounds.

The longest sections of the book are devoted to detailed accounts of "The Effect of Certain Atomic Groupings on the Specific and Selective Activity of Compounds in Inorganic Analysis" (202 pages) and "Surface Effects in Analytical Chemistry" (180 pages). It is possibly in the last-mentioned that the most stimulating observations will be found: it is intimately connected with the following chapter, entitled "Genetic Formation of Materials and Topochemical Reactions." That the results of a chemical reaction may be highly dependent upon the manner in which it is performed is, perhaps, most strikingly shown by the example of magnesite, which, when powdered, reacts immediately as a base towards saturated nickel dimethylglyoxime solution, whereas the coarse crystals do not react in this manner even if boiled with the reagent.

When considering spot tests, it is tempting to become sensational and to seek out the most sensitive reaction. Adrenaline solutions are biologically active at a dilution of 1 in 10^{18} , but the objection might be raised that this is not a purely chemical test. In the chapter on fluorescence and photochemical reactions, Feigl reports that oxine does not fluoresce in ultra-violet light, but that aluminium oxinate fluoresces strongly, so that 1 part of oxine can be detected if it is absorbed on 10^{12} parts of alumina, "which doubtless is a record." The author believes that the first accurate description of a spot test was by H. Schiff in 1859; the book under review is a striking revelation of the developments in the intervening period of nearly 100 years.

G. H. WYATT

VITAMINOLOGY. By WALTER H. EDDY, Ph.D. Pp. v + 365. Baltimore: The Williams & Wilkins Co. London: Baillière, Tindall & Cox. 1949. Price 46s. 6d. net.

This book attempts to give a comprehensive review of the more important aspects of our knowledge of the vitamins. The deficiency diseases produced by their absence are discussed, as well as the known functions of the different vitamins. Doses suggested for maintenance and therapy are given with reference to the work on which present practice is based. Chemical formulae are shown, with some indication of the metabolic processes in which the B vitamins are concerned. The toxic effects associated with large doses of certain vitamins are described.

On the whole this book gives a fair picture of our main knowledge of vitamins. It is a pity that the author states that vitamin A is of value in the treatment of "colds": there is no justification for this statement. In the chapter on vitamin D there is no reference to the use of massive doses of vitamin D in the treatment of hypoparathyroidism or lupus. The relation between vitamin D and the parathyroids is not clearly presented, although within the last ten years the work of Aub and Albright has contributed much to this subject.

A number of uncritical statements are made; for instance, on p. 87 the postulated relation between vitamin K, prothrombin and carcinogens is highly speculative. On p. 39 the use of vitamin D is suggested for a number of conditions, but the evidence that this treatment is of real value is not convincing or generally accepted.

The index is not as comprehensive as one would wish in a book of this price and pretensions. Yeast and liver only have one reference each in the index and there are no references to bacteria or fungi. In the bibliography on vitamin E, six of the references quoted are not mentioned in the text.

The book is well produced, as one would expect at the price—forty-six shillings and sixpence.

W. F. J. CUTHBERTSON

TAYLOR'S PRINCIPLES AND PRACTICE OF MEDICAL JURISPRUDENCE. Tenth Edition. Edited by SYDNEY SMITH, C.B.E., M.D., F.R.C.P., with a complete revision of the LEGAL ASPECT by W. G. H. COOK, LL.D., M.Sc., and of the CHEMICAL ASPECT by C. P. STEWART, Ph.D., M.Sc. Volume I, pp. vii + 723. Volume II, pp. vii + 841. London: J. & A. Churchill. 1948 and 1949. Price: Vol. I, 45s.; Vol. II, 50s.

The two volumes under review are the tenth edition of a well-known work which is recognised as a standard book on medical jurisprudence. It is a valuable guide not only to the medical man and the forensic scientist, but also to the lawyer when dealing with cases involving medico-legal problems.

The recent changes in the "law"—National Health Act, 1946, Public Health Act, 1936, Food and Drugs Act, 1938, Pharmacy and Medicines Act, 1941, etc.—have necessitated complete revision of certain sections to bring them up to date. Some recent decisions in the English Law Courts and the House of Lords are referred to.

The section on identification includes a review of *Rex v. Ruxton* case (1936), *Rex v. Donkin* case (1942), and a brief description of the methods of making casts of the scale pattern of hair is also included.

The section dealing with the possibilities of spontaneous combustion of the human body could with advantage be rigorously revised in the light of more up-to-date observations and conclusions.

Volume II deals, in Part I, with sexual medical jurisprudence, and Part II with poisoning and toxicology. It is this latter section which will be of particular interest to the readers of the journal for which this review is written. After a review of the Pharmacy and Dangerous Drugs Acts, the author deals with "the action of poisons and the circumstances which influence it." This is followed by observations and procedure in the case of a post-mortem examination. Since it is from such an examination that the chemist subsequently gets his materials, it is essential that the procedure outlined in this section should be followed.

Then follows a long section dealing with chemical analysis. It is, of course, a matter of opinion as to how far the subject should be developed in a work of this type. This is perhaps the most difficult section to keep up to date—new drugs are frequently being introduced, the toxicological effects of which have not as yet been fully explored; also methods for detection in the body tissues are still lacking.

On the whole, the section is very well done, the text being supported by many useful references.

There is one minor feature which might be corrected since these volumes are frequently used as reference works by non-scientific members of the Bar. The results quoted from several cases refer to arsenic calculated as arsenious oxide, *i.e.*, the actual figures quoted refer to arsenious oxide and not arsenic; this is only clearly indicated in one case from South Africa, p. 421.

There is a general improvement in the arrangement; whereas in the previous edition the two volumes were divided into fifteen sections, the sections being further divided into sub-sections, in the present edition the more usual procedure is adopted; Volume I contains eighteen and Volume II seventeen chapters, each with appropriate headings.

A feature of the volumes is freedom from errors, and the publishers are to be congratulated on their part in the production of this work.

J. B. FIRTH

THÉORIE ET MÉTHODE NOUVELLE D'ANALYSE QUALITATIVE. By G. CHARLOT. Third Edition. Pp. 328. Paris: Masson et Cie. 1949. Price 1000 fr.

This text has been almost entirely rewritten in the light of recent developments in inorganic analysis and is divided into three parts: (i) physico-chemical theory of qualitative analysis, (ii) analysis of cations and anions in solution, (iii) scheme of analysis of cations and anions.

The first 129 pages are concerned with the physico-chemical principles of qualitative analysis, and this is undoubtedly the main asset of the book. This section is admirably treated and Professor Charlot has succeeded in presenting a wide range of material in a clear and concise manner. More stress is laid upon physico-chemical principles than in most books of comparable length, and for this alone the book is to be commended. Occasionally, Professor Charlot strays into territory which is normally dealt with as quantitative analysis. Among the subjects discussed in this section of the book are: atomic structure and valency, chemical equilibrium, acids and bases (Brønsted conception), oxidation - reduction, complexes, catalysis, formation and properties of precipitates, and so on—all from the standpoint of reaction in solution.

The second part of the text (170 pages) details the reactions of cations and anions in solution, with a view to their later presentation in a new scheme of analysis. Again, much valuable and relevant information is given, of particular interest being the influence of pH on insolubility, formation of complexes, and an exhaustive and completely revised list of reaction constants for each element. The main feature of this section is the inclusion of tests for many of the less-common elements, *e.g.*, columbium, tantalum, uranium, gallium, indium, germanium, rare earths and platinum metals. Reactions of many of the less-common anions are also given.

The final part of the book (12 pages) describes an entirely new scheme of analysis. The classical tabular method of presentation is abandoned in favour of a somewhat novel procedure incorporating pH control methods, organo-inorganic complex formation, and redox reactions. Precipitants successively used in the scheme of cation analysis are sodium sulphide, cupferron, α -benzoinoxime and ammonium sulphate. The proposed cation tests are not intended for the detection of trace amounts of elements, but rather for the more rapid and simple detection of ions present in appreciable amounts. Accordingly, reactions less sensitive but more selective than those normally applied in microchemical methods are used.

The reviewer is of the opinion that this new scheme of analysis will not be favourably received by analytical chemists, though Professor Charlot has made an earnest and commendable attempt to break away from traditional practice.

The book undoubtedly provides a thorough physico-chemical approach to qualitative analysis—indeed, the best the reviewer has yet seen—and it is to be hoped that an English translation will soon be available.

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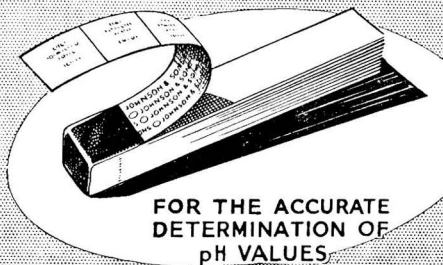
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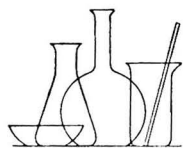
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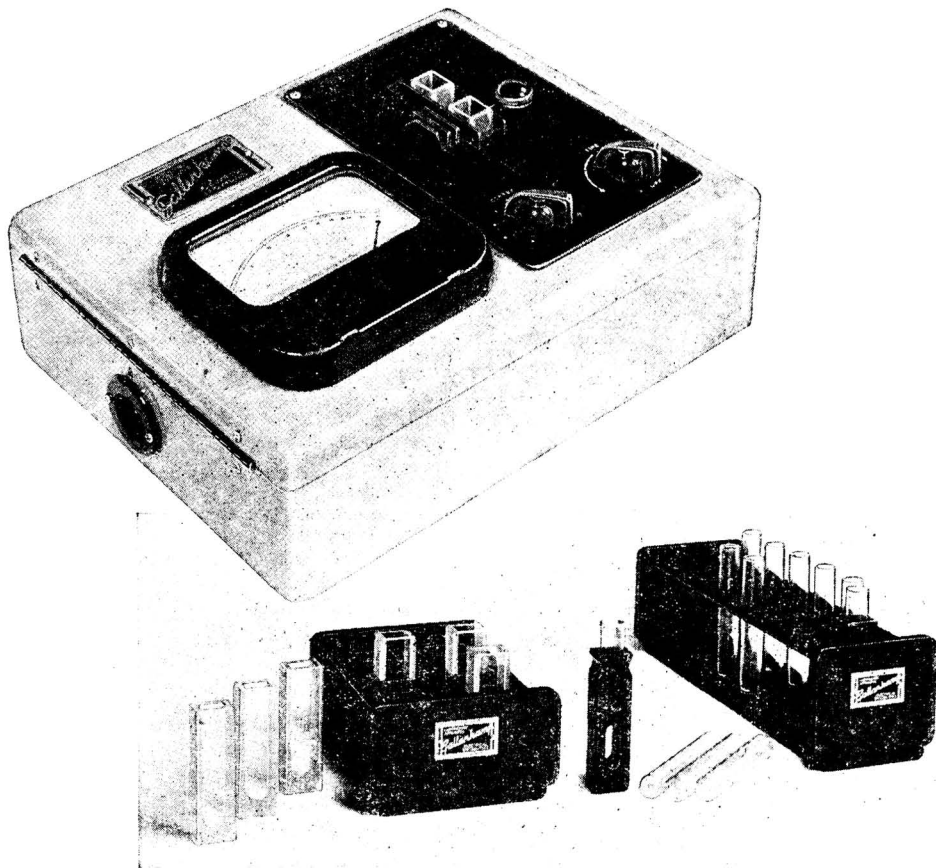
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