

# **Bromide in Waters High Level Titrimetric Method 1981**

**Methods for the Examination of Waters and Associated Materials**

# **Bromide in Waters**

## **High Level Titrimetric Method 1981**

### **(Tentative)**

#### **Methods for the Examination of Waters and Associated Materials**

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# Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; and 'Safety in Biological Laboratories (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decon-

tamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt; it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

# About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee

of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

- 1.0 General principles of sampling and accuracy of results
- 2.0 Instrumentation and on-line analysis
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General nonmetallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 8.0 Sludge and other solids analysis
- 9.0 Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

**T A DICK**  
*Chairman*

**L R PITTWELL**  
*Secretary*

*4 December 1980*

# Bromide in Waters

## High-Level Titrimetric method (tentative)

### 1981

*Note:* Throughout this method bromide is expressed as the ion  $\text{Br}^-$ . Since the procedure was developed primarily for sea water, for which the preferred unit for this component is mg/kg, performance characteristics are expressed in terms of these units. For a low level method, see another booklet in this series.

#### 1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results, also published in this series)

1.1	Substance determined	Soluble bromide ion		
1.2	Type of sample	Water including sea water.		
1.3	Basis of method	Oxidation of bromide to bromate, followed by iodometric determination.		
1.4	Range of application	up to 140 mg/kg		
1.5	Standard deviation	(a) Wt. (in mg) of added bromide per 10g of sample	Bromide conc. found mg $\text{Br}^-$ /kg	Within-batch Standard Deviation mg $\text{Br}^-$ /kg
		0.0000(b)	0.02	0.02
		0.6954(c)	69.53	0.11
		0.6954(d)	69.47	0.03
		0.0000(e)	61.71	0.06
		0.6954(f)	131.13	0.09
		0.0000(g)	60.58	0.12
		0.0000(h)	62.30	0.04
		(b) Distilled water; 6 degrees of freedom		
		(c) Spiked distilled water, 6 degrees of freedom. Mean recovery = 99.98%.		
		(d) Spiked distilled water; 6 degrees of freedom; a different operator. Mean recovery 99.90%		
		(e) Sea water; 6 degrees of freedom		
		(f) The same sea water spiked with 0.6954 mg $\text{Br}^-$ /10 g; 6 degrees of freedom. Recovery = 99.86%.		
		(g) Sea water (chlorinity = 19.50‰);		
		(h) Sea water, a different operator.		
1.6	Limit of detection	0.09 mg/kg (6 degrees of freedom)		
1.7	Bias	Recovery tests on sea water gave no evidence of bias (see footnote to section 1.5)		
1.8	Interferences	Iodide, some oxidizing and reducing agents, see Section 3		
1.9	Time required for analysis	A typical time for the analysis of 10 samples is 2.5 hours.		

(a) Based on data obtained in the Department of Oceanography, University of Liverpool using a 10 ml sample volume.

## 2 Principle

The method is an adaptation (1, 2) of a technique developed by Kolthoff and Yutzy (3) and modified by Haslam and Moses (4). Bromide is oxidized to bromate by sodium hypochlorite at about 100 °C in a medium buffered to pH 6.2 with phosphate. After reduction of the excess oxidant with formate, the bromate is determined iodometrically.

## 3 Interferences

Bromate is recorded as bromide. Iodate and iodide are recorded as their equivalents in bromide. If oxidizing agents or reducing agents stable on boiling with hypochlorite and treatment with formate ion are present in quantity they will cause problems with the method. Table 1 gives details of potential interfering substances which have been tested.

Table 1

Effect of other substances on the determination of bromide (a)

Other substance	Substance added as	Concentration of other substance mg/1	Effect of other substance in mg/1 Br at a bromide concentration of 69.54 mg/1
Bromate (as Br <sup>-</sup> )	Potassium salt	69.54	+69.49 (b)
Chlorate (as ClO <sub>3</sub> <sup>-</sup> )	Potassium salt	20.0	-0.05
Chromate (as CrO <sub>4</sub> <sup>2-</sup> )	Potassium salt	10.0	- 0.02
Copper (II) (as Cu)	Chloride	1.0	-0.02
Iron (III) (as Fe)	Chloride	1.0	-0.02
Manganese (II) (as Mn)	Chloride	1.0	-0.08
Nickel (II) (as Ni)	Chloride	1.0	0.00
Nitrate (as NO <sub>3</sub> <sup>-</sup> )	Potassium salt	100.0	-0.08
Nitrite (as NO <sub>2</sub> <sup>-</sup> )	Sodium salt	10.0	-0.06
Sulphite (as SO <sub>3</sub> <sup>2-</sup> )	Sodium salt	20.0	-4.97

(a) These determinations were carried out in distilled water spiked with the stated concentrations of other substances using the procedure given in Section 8.1

Data obtained in the Department of Oceanography, University of Liverpool.

If the other substances had no effect, the results would be expected (95% confidence) to lie within the following range

$$0.00 \pm 0.10 \text{ for } 68 \text{ mg Br}^{-}/1$$

(b) mean of 5 determinations, standard deviation 0.03 mg/1.

## 4 Hazards

Formic acid is toxic and corrosive.

## 5 Reagents

Analytical reagent grade chemicals should be used unless otherwise recommended.

### 5.1 Water

The water used for blank determinations and preparation of reagents and standard solutions should have a bromide content which is negligible compared with the lowest concentration to be determined in the samples. Deionized or distilled water are normally suitable.

## 5.2 Phosphate buffer

Dissolve  $5.0 \pm 0.2$  g of sodium dihydrogen orthophosphate in water and dilute with water to  $100 \pm 2$  ml. Store the solution in a glass bottle. It is stable indefinitely.

## 5.3 Sodium chloride (10% m/V)

Dissolve  $100 \pm 1$  g of sodium chloride in water and dilute to  $1000 \pm 20$  ml with water. It is stable indefinitely.

## 5.4 Sodium hypochlorite solution (Approx. 0.5 M)

A grade of 1.0 M sodium hypochlorite in 0.1 M sodium hydroxide having a low bromide content should be used. The reagent should be stored at 4 °C and not used after the expiry date given by the manufacturer.

## 5.5 Formic acid 90% m/m

## 5.6 Sodium formate solution

Carefully dissolve  $30 \pm 1$  g of sodium hydroxide in  $150 \pm 2$  ml of water. Cool in an ice bath and then add cautiously, with stirring,  $32 \pm 1$  ml of 90% m/m formic acid. Dilute to  $200 \pm 2$  ml with water. This reagent should be stored in a glass bottle; it is stable indefinitely.

## 5.7 Potassium iodide

## 5.8 Ammonium molybdate solution (3% m/V)

Dissolve  $3.0 \pm 0.1$  g of ammonium molybdate in water and dilute with water to  $100 \pm 2$  ml. Store the solution in a polyethylene bottle, reject it if a sediment begins to form.

## 5.9 Sulphuric acid (3M)

Carefully add  $41 \pm 1$  ml of sulphuric acid ( $d_{20}$  1.84) to 200 ml of water while cooling. Dilute to  $250 \pm 2$  ml with water. See Section 9.4.

## 5.10 Standard potassium bromate solutions

### 5.10.1 Solution A (0.01667 M equivalent to 0.1N)

Dry potassium bromate overnight at 110 °C. Weigh out  $2.7845 \pm 0.0010$  g of the dried salt, dissolve in water and dilute to 1 l in a calibrated flask. Store the solution in a well stoppered amber glass bottle; it is stable for at least 4 months.

### 5.10.2 Solution B (0.0003333 M equivalent to 1/500 N)

Pipette 20 ml of the potassium bromate solution (5.10.1) into a 1 l calibrated flask and dilute to volume with water. This solution should be prepared freshly as required.

## 5.11 Standard sodium thiosulphate solutions

### 5.11.1 Solution A (approx 0.1 M)

Dissolve  $25 \pm 1$  g of sodium thiosulphate in water and dilute to 1 l with water. Store the solution in an amber glass bottle; it is stable for up to a month.

### 5.11.2 Solution B (approx 0.002 M)

Pipette 20 ml of the stock thiosulphate solution (5.10.1) into a 1 l calibrated flask and dilute to volume with water. This reagent is unstable and should be prepared each day as required.

## 5.12 Starch solution

Add a suspension of  $0.5 \pm 0.2$  g of soluble starch in  $10 \pm 2$  ml of water to about 150 ml of boiling water. Boil for 1 – 2 minutes and then cool. It is essential that this reagent is prepared fresh daily. Proprietary brand indicators for iodine may also be suitable.

## 6 Apparatus

Before and after use all apparatus should be well washed with water.

## 7 Sample Collection and Preservation

Samples can be taken in either glass or polyethylene bottles which have been well washed with water. No preservative is necessary. Tests have shown that bromide at 40 mg/l is stable for several years in glass or polyethylene containers.

## 8 Analytical procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
8.1	<b>Analysis of samples</b> Pipette 10 ml of the sample (Note a) into a weighed 250 ml conical flask and reweigh ( $\pm 0.005$ g)	(a) This volume is suitable for sea water but can be increased to 20 ml with samples containing lower concentrations of bromide if results are expressed in mg/l the weighing can be omitted.
8.2	Add $10.0 \pm 0.5$ ml of phosphate buffer (5.2) $10 \pm 1$ ml of sodium chloride solution (5.3) and $2.0 \pm 0.1$ ml of sodium hypochlorite solution (5.4). Dilute to $40 \pm 5$ ml with water. Heat the solution to boiling on a hot plate and boil for 2 to 4 minutes. Allow to cool for about 30 seconds and then add $10.0 \pm 0.5$ ml of sodium formate solution (5.6). Mix well and cool to room temperature.	
8.3	Add $0.25 \pm 0.02$ g of potassium iodide (5.7), 2-3 drops of ammonium molybdate solution (5.8) and $10.0 \pm 0.5$ ml of 3 M sulphuric acid. (5.9). (Note c). Mix well and titrate immediately with the thiosulphate solution B (5.2) to a very pale straw colour. Add 1–2 ml of starch solution and continue the titration until the blue colour of the starch-iodine complex is just discharged. (Notes b and d).	(b) To avoid photochemical oxidation of iodide ion the titration should be carried out under subdued lighting. (c) See Section 9.4. (d) The solution should remain colourless for at least $\frac{1}{2}$ min; the colour will, however, slowly return.
	<b>Blank determination</b>	
8.4	A blank must be run with each batch of determinations using the same batch of reagent as for the samples. Transfer $10 \pm 2$ ml of water to a 250 ml conical flask and then carry out Steps 8.2 and 8.3.	
	<b>Standardization of thiosulphate solution B</b>	
8.5	Pipette 40 ml of potassium bromate solution B (5.10.2) into a 250 ml calibrated flask. Proceed to Step 8.3. Carry out a corresponding reagent blank in the same manner using 40 ml of water instead of the bromate solution.	
	<b>Calculation of results</b>	
8.6.1	Molarity of thiosulphate (M) = $\frac{40 \times 0.002}{(V_s - V_{bs})}$ Where $V_s$ = volume of thiosulphate used in the titration of the iodine liberated from 40 ml of 0.0003333 M bromate solution in Step 8.3 and $V_{bs}$ is the corresponding reagent blank.	



### 8.6.2 Bromide content of sample

$$\text{in mg/kg} = \frac{(A - B) \times M \times 79.91 \times 1000}{6 \times W}$$

Where:

A = sample titre in millilitres of thiosulphate of molarity M

B = the corresponding reagent blank (Step 8.4)

W = weight in grams of sample taken (normally about 10g)

8.6.2.1 If the bromide concentration is required in mg/l substitute the volume in millilitres of sample taken in step 8.1 (usually 10 or 20 ml) for W in the formula above.

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## 9 Sources of error

9.1 See section on interferences

9.2 Errors may occur in both the determination and the standardization of the thiosulphate through loss of iodine by volatilization. It is essential to proceed with the titration without delay after the addition of potassium iodide and acidification (Step 8.3).

9.3 Photochemical oxidation of iodide ion may occur if the titration is carried out in direct sunlight.

9.4 The use of sulphuric acid containing oxidizing impurities may give rise to unacceptably high blanks. Analytical reagent grade acid is normally satisfactory.

## 10 Accuracy of Results

Analytical quality control procedures are recommended. Suitable procedures are described in references 5-7.

## 11 References

- (1) Morris AW and Riley JP, *Deep-Sea Res.* 13. 1966, 699-705.
- (2) Morris AW, *Ph.D. Thesis*, University of Liverpool, 1965.
- (3) Kolthoff IM and Yutzky H, *Ind. Engng. Chem., (Anal)* 9. 1937 75-80.
- (4) Haslam J and Moses G, *Analyst*, 75, 1950, 343-50.
- (5) Cheeseman RV, and Wilson A.L Water Research Centre *Technical Report TR66*. Medmerham 1978.
- (6) Dewey D, *Analyst* 104, 290-298. 1979.
- (7) *General Principles of Sampling and Accuracy of Results 1980*, HMSO London.

## Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this booklet are requested to write to:

The Secretary  
The Standing Committee of Analysts  
The Department of the Environment  
2 Marsham Street  
LONDON SW1P 3EB  
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# Department of the Environment/National Water Council

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