The Determination of Iodine, Iodate, Iodide and Traces of Bromide in Waters 1984 (Tentative Methods)

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Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.75 net

The Determination of Iodine, Iodate, Iodide and Traces of Bromide in Water 1984

Methods for the Examination of Waters and Associated Materials

This booklet contains a method for total inorganic iodine and a method for iodate. With these two methods it is usually possible to speciate any iodine present. Free iodine is rarely encountered, but can be removed by extraction in carbon tetrachloride. A note on methods for the determination of traces of bromide with information on applicability is also included at the end of the booklet, in most instances an HPLC method is preferred.

Contents

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Warning of 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 whether for one's self, one's colleagues in the laboratory, outsiders or subsequently for maintenance workers. 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 specifications. 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; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection, 'Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care must be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasized that prompt first aid, decontamination, 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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.

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About this series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, 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, have 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 the 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 a committee of the Department of the Environment set up in 1972. Currently it has seven 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
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods.

The actual methods and reviews 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.

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 and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. 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 that booklet.

L R PITTWELL
Secretary

31 October 1983

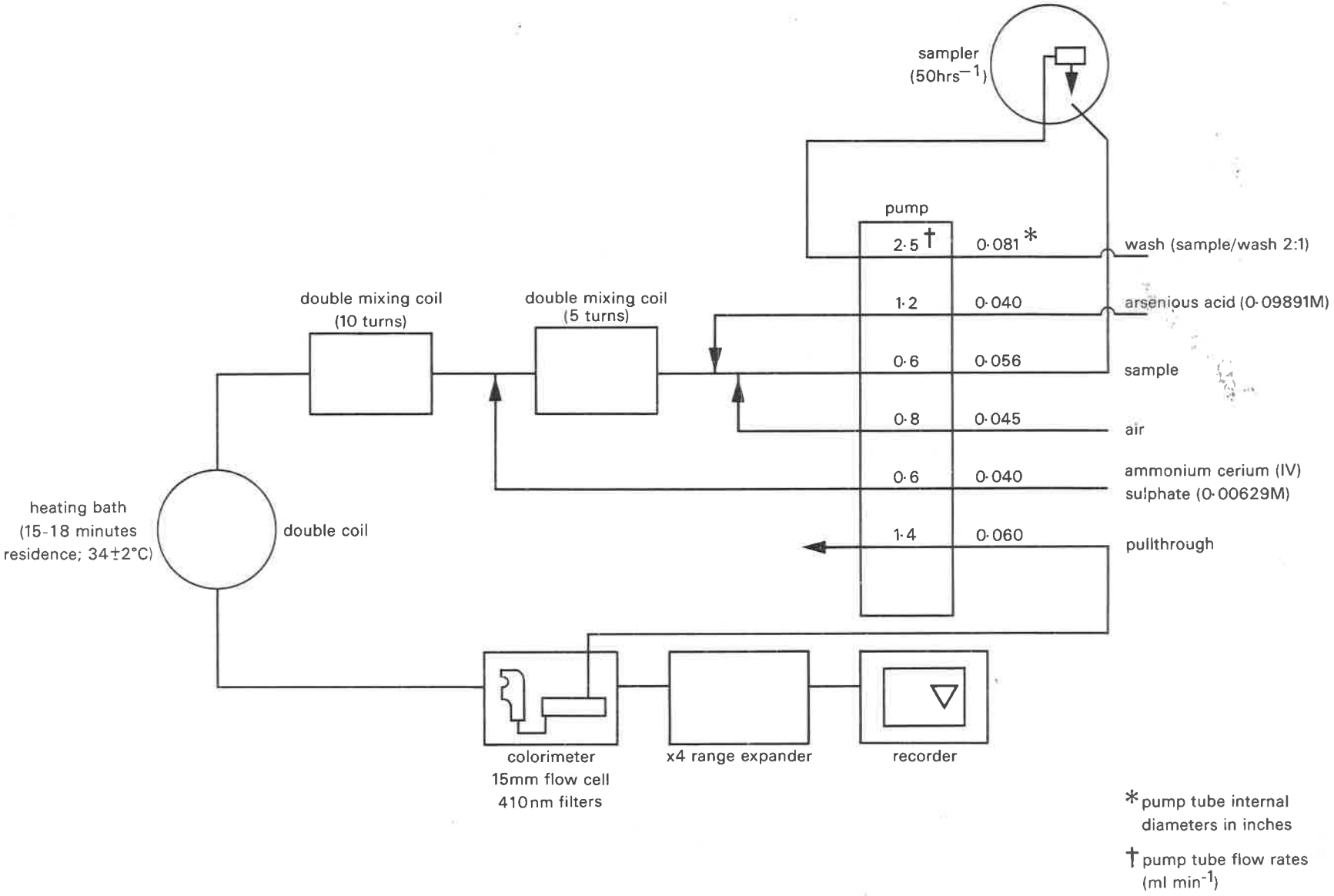

FIGURE 1 THE AUTOANALYSER MANIFOLD FOR THE TOTAL INORGANIC IODINE PROCEDURE

Iodine in Waters by Automated Catalytic Spectrophotometry (Tentative)

Introduction

Iodate and iodine are the principal forms of dissolved iodine found in natural fresh waters. Accoding to theoretical chemical oxidation/reduction considerations, iodate would be expected to be the only form of inorganic iodine in oxygenated waters, whereas only iodide could be expected to be present in anoxic waters. However, the biological reduction of iodate to iodide and the slow rate of oxidation of iodide, allows iodide to persist in oxygenated waters. Analysis of natural waters therefore requires methods for the determination of each form of iodine. The existence of molecular iodine and organic iodine compounds have not so far been reported in solution in fresh waters.

Two methods are given, one for total inorganic iodine, ie iodate and iodide (Method A) and the other for iodate only, iodide being calculated by difference (Method B).

See also Section 5 under Determination of Traces of Bromide in Waters

Method A: Total Iodine in Water by Automated Catalytic Spectrophotometry (Tentative)

A1 Performance Characteristics

A1.1	Substance determined	Inorganic iodine including some organic iodine compounds.
A1.2	Type of Sample	Raw and potable waters.
A1.3	Basis of Method	Catalytic effect of iodide on the reduction of Cerium (IV) ammonium sulphate by arsenic (III) oxide.
A1.4	Range of application	Up to 5 μg/l
A1.5	Calibration curve	Linear to 5 μg/l in the ×4 expanded mode (non linear when not expanded, see Reference 2).
A1.6	Standard Deviation (a) (within-batch estimates)	

Iodine Concentration	Standard Deviation	Degrees of Freedom
μg/l	μg/l	
1.0	0.035	11
2.0	0.057	11
3.0	0.101	11
4.0	0.104	11
5.0	0.107	11

A1.7	Limit of Detection (a)	0.2 μg/l (11 degrees of freedom).
A1.8	Sensitivity (a)	1.0 μg/l I gives a change in transmission of 12.9% in the ×4 expanded mode.
A1.9	Bias	Not known
A1.10	Interferences	Reducing agents, sample colour and turbidity (see Sections A3 and A8.7)
A1.11	Time required for analysis (a)	Setting up time 30 minutes and then up to 50 determinations per hour.

(a) These data were obtained at the Institute of Hydrology without using the sample blank correction in Section A8.7.

A2 Principle

A2.1 Iodide-iodine catalyses the reduction of cerium (IV) ammonium sulphate by arsenic (III) oxide, and the iodide concentration is related to the increase in the rate of this reaction (1, 2). The calibration curve is mathematically complex but approximates very closely to a linear model over the range 0–5 μg/l when using a colorimeter reading in % transmission and in the ×4 expanded mode.

A2.2 Iodate and other oxidized iodine species are converted to iodide on mixing with the large excess of arsenic (III) reagent before the addition of the cerium (IV) salt. Some organic iodine compounds, eg 3,5 di-iodotyrosine respond as though inorganic iodine.

A2.3 The method may need to be adapted for other types of automatic analysis equipment which may include colorimeters reading in absorbance units. In this case the analyst should consult References 1 and 2 and note that the optimization of kinetic methods is different in principle from that of direct colorimetric methods. For a general treatment of the optimization of kinetic methods of analysis see Reference 3.

A3 Interferences

Sample colour and/or turbidity interfere causes the results to be falsely low whereas reducing agents have the opposite effect. The effect of some reductants are shown in Table 1. In general, the method responds differently to different reductants, the degree of interference depending on the particular reducing agent present and its concentration. Nevertheless, the response of the method to a sample containing iodine and reductant is shown to be additive for those tested. (Table 1). Therefore, this interference can be circumvented by estimating the concentration of the reductants in samples by means of a blank procedure (see section A8.7).

Table 1

Reductant	Concentration (mg/l)	Effect in μg/l I at I concentration of		
		0 μg/l	2 μg/l	5 μg/l
Fe^{2+}	20	+ 1.6	+ 1.6	–
SO_3^{2-}	50	+ 1.5	–	+ 1.5

A4 Hazards

The arsenic III oxide and its solution is toxic. Sulphuric acid is corrosive. The precautions given in the essay review on continuous flow analysis should be observed (4).

A5 Reagents

A5.1 Water Consistent results have been obtained using deionized, distilled water. The conductivity of this water must be less than 0.5 μ mhos/cm.

A5.2 Standard Iodide Solution 1 ml contains 100 μg I. Dry sodium iodide for about 1 hour at 110°C. Dissolve 0.118 ± 0.0005 gm of the solid salt in 1 litre of deionized distilled water to give a solution containing 100 mg/l of I. Stable for several months.

A5.3 Intermediate Standard Iodide Solutions. 1 ml contains 1 μg I. Dilute 1.0 ml of the stock solution A5.2 to 100 ml with deionized, distilled water in a volumetric flask. This solution is stable for at least 1 month when stored in a polypropylene bottle.

A5.4 Cerium IV reagent. Dissolve 3.75 ± 0.1 gm of the yellow solid salt [2 $(NH_4)_2 SO_4$. $Ce(SO_4)_2$. 3½ H_2O] in 200 mls of distilled water. Add 52 ± 1 ml of concentrated sulphuric acid (18.6M) and then make up to 1 litre with distilled water. Filter the solution through a glass fibre filter (GF/C) before use.

A5.5 Cerium IV reagent for blank determinations. Dissolve 1.5 ± 0.1 gms of the yellow solid salt in 200 mls of distilled water. Continue as in A5.4 (Note: this reagent is used without the arsenic reagent and the lower cerium concentration is necessary in order to yield the same base-line setting as that in the catalytic procedure).

A5.6 Arsenic III oxide. Dissolve 19.6 ± 0.1 gm of arsenic III oxide plus 14.0 ± 0.1 gm of sodium hydroxide in a small amount of distilled water. Dilute the solution with a further 600 ml of distilled water. Add concentrated sulphuric acid (18.6M) dropwise until neutral to phenolphthalein.

Add a further 56 ± 1 ml of the concentrated acid and 50 ± 0.1 gm of sodium chloride, before making the volume up to one litre with distilled water. Filter the solution through a GF/C glass fibre filter.

A6 Apparatus

A6.1 An automatic continuous flow analyser, consisting of

A sample presentation unit
A peristaltic pump
A chart recorder
A heating bath with thermostating to ± 0.05°C and equipped with a long delay coil (15–18 mins), in which the reaction mixtures can be incubated.

An analytical manifold as shown in Figure 1.

A6.2 In addition the following are required:

A colorimeter reading in % transmission and a ×4 range expander for the colorimeter/recorder.

Note: The test data given with this method were obtained using a Technicon Auto-analyser I colorimeter with a 15mm flow cell. If other types of colorimeter are used, such as those reading only in absorbance units, it may be necessary to change the analytical manifold from that shown in Figure 1. For more detailed information on how to adapt the procedure for use with other types of colorimeter the analyst should consult the references given.

A7 Sample Collection and Preservation

Samples can be collected in glass bottles and stored for up to 1 week without deterioration.

A8 Analytical Procedure

Step	Procedure	Notes
	Starting Operation	
A8.1	Assemble the apparatus as shown in Figure 1, with the heating bath at approximately 35°C (note a) and the colorimeter at 410 nm (15mm flowcell).	(a) Ensure the heating bath is equipped with a thermostat capable of temperature control to ± 0.05°C.
A8.2	While aspirating only the arsenic reagent and deionized, distilled water, set 0 and 100 per cent transmission on the recorder (note b).	(b) Follow the manufacturer's general operating instructions.
A8.3	Introduce the cerium IV reagent, this establishes the baseline between 31% and 35% transmission (absorbance 0.45–0.5) (note c).	(c) When necessary, small shifts in the base line position may be effected by altering the temperature of the heating bath (± 2°C or by an appropriate change in the original Ce IV concentration.
	Initial Sensitivity Setting	
A8.4	When the baseline has settled within this transmission range expand the 30–55% transmission interval to full scale using the ×4 range expansion facility. Adjust the baseline to 5% apparent transmission (notes d and e).	(d) Follow the manufacturer's recommended procedure. (e) Allow the system to equilibriate for 15 minutes and during this period check for baseline drift and ensure a satisfactory bubble pattern. Eliminate difficulties before proceeding to A8.5.
	Analysis of standards and samples	
A8.5	Calibration standards (0–5 μg/l I) In a series of five 100 ml volumetric flasks pipette 0.1 0.2, 0.3, .0.4 and 0.5 ml of intermediate standard iodide solution (A5.3). Dilute to the mark with deionized distilled water to provide calibration standards of 1.0 to 5.0 μg/l I. These solutions are stable for at least one week.	

Step	Procedure	Notes
	Load the sample turntable in the following order (notes f and g).	(f) The turntable can be loaded during the initial stabilization period.
		(g) This order is a suggestion. Other loading patterns may be used (3).

position	solution
1–5	calibration standards in ascending order.
6–9	blank (note h).
10–20	samples
21	calibration standard
21–22	blank
23–33	samples
34–39	calibration standards in descending order.
40	blank (note i).

(h) This must be deionized, distilled water from the same batch as used for the calibration standards.

(i) Check on baseline drift. Adjust if necessary between sample trays to maintain 5% apparent transmission.

Aspirate sample and blanks at the rate of 50 per hour.

Repeat the sequence 6–40 until all the samples have been processed.

A8.6 Remove the arsenic and cerium reagents and pump out the manifold with deionized, distilled water.

Determination of sample blanks

A8.7 Where the presence of reducing agents in samples is suspected introduce the cerium reagent used for blank determination and re-establish a baseline at 5% apparent transmission as described in A8.4. (note j).

(j) Omit this procedure if reducing agents are known to be absent.

Shut down procedure

A8.8 Remove the cerium reagent (blanks) and pump out all pump tubes with deionized distilled water for 30 mins. Turn off the pump and release the pressure in the pump tubes.

A9 Calculation

A9.1 Read off the peak height (%T) of the standards relative to the baseline and construct a calibration graph. Similarly, read of the peak heights of samples and sample blanks using the response to deionized distilled water as datum. Subtract the peak-height of the sample blank from the peak-height of the sample, and by comparing the result with the calibration curve ascertain the sample total iodine concentration.

A10 Sources of Error

A10.1 Vigilance should be exercised when anoxic/reducing waters are being analysed. In particular, the co-precipitation of Iodide-Iodine with ferric hydroxides produced when these waters are oxygenated during analysis, may lead to anomolous total iodine concentrations. If necessary prevent precipitation or redissolve with the minimum addition of sulphuric acid to the sample. Include a similarly treated blank.

A10.2 Kinetic methods of analysis are particularly sensitive to changes in reaction times and temperature. Inadequate control of these factors will lead to a marked deterioration in precision. The analyst should note that the sample blank correction (A8.7) is an additional source of error and that the test data were obtained without using this stage in the procedure.

Method B. Separate Determination of Iodate and Iodide in Water (Tentative).

B1 Performance Characteristics

B1.1	Substance determined	Soluble iodate and iodide.
B1.2	Type of Sample	Raw and potable waters.
B1.3	Basis of Method	Total inorganic iodide is determined by Method A. This is repeated, after extraction of iodide with tetraphenyl ammonium hydroxide and chloroform, to determine iodate. Iodide is obtained by difference.
B1.4	Range of Application	Up to 5 μg/l as either iodide or iodate.
B1.5	Calibration Curve.	Linear to 5 μg/l (see Method A).
B1.6	Standard Deviation (a) (within batch estimates).	Standard solutions of iodate/iodide:—

Iodate/Iodine concentration	Standard Deviation	Degrees of Freedom
μg/l	μg/l	
0.0	0.10	5
1.0	0.12	5
2.0	0.12	5
3.0	0.07	5
4.0	0.10	5
5.0	0.07	5

Iodide Iodine concentration	Standard Deviation	
1.0	0.14	5
2.0	0.14	5
3.0	0.12	5
4.0	0.14	5
5.0	0.12	5

B1.7	Limit of Detection	Iodate Iodine: 0.2 μg/l Iodide Iodine: 0.3 μg/l
B1.8	Sensitivity	1.0 μg/l Iodate iodine gives a change in transmission of 12.6% in the ×4 expanded mode.
B1.9	Bias.	Not known.
B1.10	Interference	As for Method A and Section B3.
B1.11	Time required for analysis	10 samples per hour for total inorganic iodine, iodate and iodide.

Note (a) These date were obtained at the Institute of Hydrology.

B2 Principle

Iodide ions are paired with the tetraphenylarsonium cation and the ion-pair formed extracted from the aqueous phase into chloroform. The concentration of iodate — iodine and iodide — iodine in mixtures of the two can be measured by determining the total iodine concentration, both before and after removal of the iodide — iodine component (2).

Reactive organic iodine compounds (see section A2.2) may respond as either iodate or iodide depending on their solubility in chloroform. Those soluble in chloroform are determined as iodide, those insoluble in this solvent, as iodate.

B3 Interferences

The results for iodate will be sensitive to those substances which interfere with catalytic method for total inorganic iodine and which are also not extractable by chloroform in the presence of tetra phenylarsonium ions.

The effect of various ions in the determination of iodate and iodide was given in Table 2. A solution containing 3.0 μg/l iodide and 2.0 μg/l of iodine as iodate was used.

Table 2

Substance Added	Concentration (mg/I)	Measured Concentration of Iodine Species (μg/l)		
		I Total	IO_3^-	I^-
Cl^-	300	5.0	2.0	3.0
NO_3^- N	30	5.0	1.9	3.1
PO_4^{3-} P	100	5.0	2.0	3.0
SO_4^{2-}	100	5.0	2.1	2.9
HCO_3^-	100	5.0	2.0	3.0
Ca^{2+}	100	5.0	2.1	2.9
Mg^{2+}	100	5.0	2.0	3.0
K^+	100	5.0	1.9	3.1
Na^+	100	5.0	1.9	3.1
Fe^{2+}	0.1	5.0	2.2	2.8
Fe^{3+}	0.1	5.0	2.1	2.9
Cu^{2+}	0.1	5.0	2.1	2.9
Mn^{2+}	0.1	5.0	2.2	2.8
Ni^{2+}	0.1	5.0	2.0	3.0
Br^-	15	5.0	1.9	3.1
SiO_4^{4-}	15	5.0	1.8	3.2

If the other substances did not interfere, the responses to I total, IO_3^- and I– 95% confidence) would be expected to lie between 5.00 ± 0.1, 2.0 ± 0.1 and 3.0 ± 0.14 μg/l I, respectively.

In addition, the method has been found to tolerate up to 50 μg/l as $CaCO_3$ of acidity or alkalinity (0.01N) when added to samples before analysis.

B4 Hazards

Tetraphenylarsonium chloride hydrochloride and arsenic III oxide are poisons. See also hazards for total iodine method. Chloroform is both an anaesthetic and analgesic.

B5 Reagents

B5.1 Water: Deionized, distilled water has been found satisfactory.

B5.2 Standard Iodine Solutions: See Method A.

B5.3 Tetraphenylarsonium hydroxide (0.2M): Dissolve 4.55 ± 0.1 gm of solid Analytical Reagent grade tetraphenylarsonium chloride hydrochloride in 50 ml of distilled water. Add 2.0 ± 0.1 gm of silver oxide and stir the solution overnight. Filter the solution through a glass fibre filter (GF/C), before use and store in a dark glass bottle.

B5.4 Chloroform: Analytical Reagent grade.

B6 Apparatus

B6.1 Glass separatory funnels (125 ml)
a centrifuge capable of an R.C.F. of 4.5×10^4
30 ml centrifuge tubes.

B6.2 An automatic continuous flow analyser for the determination of total inorganic iodine. (A6.1 and A6.2).

B6.3 Glass sample holders for use with the automatic analyser B6.2.

B7 Sample Collection and Preservation

Samples can be collected in glass bottles and stored for up to one week at room temperature without deterioration. Filtration through washed cellulose ester or glass fibre filters does not affect the iodide — I or iodate — I determinations, significantly.

B8 Analytical Procedure

Step	Procedure	Notes
	Determination of total inorganic iodine	
B8.1	Determine the total iodine content of an untreated sample by the method A.	
	Determination of iodate-iodine	
B8.2	Pipette a 20.0 ml aliquot of sample into a clean glass separatory funnel. Add 0.1 ± 0.01 ml of the 0.2M tetraphenylarsonium hydroxide reagent. Shake the mixture. Add 4.0 ml of chloroform and shake for 2.0 ± 0.2 mins (note a). Allow the two phases to separate for 10 ± 1 mins before removing the organic phase. With a further 4.0 ml of chloroform repeat the above procedure, Centrifuge the residual aqueous phase at 4.5×10^4 R.C.F for 15 ± 2.0 mins. Decant the aqueous phase into 2.0 ml glass sample cups and determine the total iodine content by method A.	(a) Use of an automatic dispensing pipette is recommended
	Reagent Blank	
B8.3	Prepare a reagent blank using distilled water which has been treated with both tetraphenylarsonium hydroxide and chloroform as in steps B8.1 and B8.3. The response of the total iodine method (method A) to this solution is the reagent blank. Subtract this response from that obtained for the extracted samples from step B8.2 and obtain the iodate-iodine content of the sample as for method A. (note b).	(b) This procedure uses the calibration curve in method A prepared with standard iodide solutions.
	Determination of the Iodide-iodine	
B8.4	Subtract the iodate-iodine concentration from steps B8.2 and B8.3 for the total iodine concentration (step B8.1) (note c).	(c) It may be desirable to check the calibration and recovery with standard solutions which have been treated as in steps B8.2. In this case standards must be prepared from potassium iodate instead of sodium iodide.

B9 Sources of Error

Competition from other anions for the ion-pairing reagent would result in incomplete extraction of iodide-iodine from samples. This interference may be significant when analysing waters of high ionic strength.

If free iodine is present, it too will extract in chloroform and be counted as iodide. This can be corrected for by prior extraction of an aliquot of the sample with chloroform. Analysis of this portion excludes free iodine; but some organoiodine compounds will also be extracted if present.

Determination of Traces of Bromide in Waters

Preferred Method:

Occurrence

Bromine usually occurs in water as bromide, free bromine reducible to bromide may occur occasionally in effuents. Organobromine compounds which occur in nature, a few effluents and some treated waters are not included in this method.

For most purposes the preferred method is either neutron activation (see Ref 7), or Anion Exchange High Performance Liquid Chromatography using an Amperometric Detector (see below and Ref 6), which appears to be free from major interferences other than substances co-ordinating bromide so that it is no longer present as free ion. This method, is capable of determining at least as low as 20μg/l and with most samples concentration by evaporation is possible. Four other methods were also studied and found to have problems with interference effects. These are summarized in Table 3 below.

Procedure:

1. Set up the HPLC apparatus, with an amperometric detector according to the makers' instructions, choosing anion exchange or other column recommended for the separation of bromide.
2. For very low concentrations of bromide consider whether an extra large sample injection or prior partial evaporation by a known amount is advisable.
3. Standardize the instrument using a potassium bromide solution of suitable concentration (1.489 g K Br is equivalent to 1.000 g Br^-).
4. Run the samples according to manufacturers' instructions. Indentify and measure the bromide peak heights against base line; obtain the concentration by proportionation of sample and standard peak heights, allowing for any prior sample concentration. If necessary confirm by making a standard addition of a known amount of potassium bromide.

   Note, if y ml of an x mg/l solution is added to b ml of an a mg/l solution the resultant concentration is $\frac{xy + ab}{y + b}$ mg/l.
5. It is usually possible to analyse simmultaneously in succession for other ions including the other halides on the one sample. Analysts are advised to check for possibilities and interferences using synthetic samples and spiked samples. (see Reference 6).

Performance Characteristics

For Range, Limit of Detection and Interferences see Table 3. Standard Deviation and the other parameters are highly dependent on the Instrumentation and sample type; but relative standard deviations of 10% should be achievable.

Table 3

Summary of Procedures Considered

Summary of Procedure	Approximate Limit of Detection	Interferences	Modifications Possible
Preferred Procedure			
1. Anion Exchange HPLC with Amperometric Detector (see Ref 6).	5–20 μg/l dependent on size of sample injection.	Substances co-ordinating bromide which are not removable.	i) Size of sample injection ii) concentration by partial quantitative evaporation. iii) removal of interfering metals by electrodeposition iv) reduction of bromate or bromine to bromide by FeII, CrII or Ti III.
Other Procedures:			
2. Anion Exchange HPLC with Conductimetric Detector	50–200 μg/l dependent on size of sample injection.	Nitrates. High relative concentrations of Chloride may also overlap the bromide peak.	As above
3. Automated catalytic oxidation of iodine to iodate by acid permanganate and measurement of residual iodine by extraction into carbon tetrachloride and spectrophotometry at 520 nm. (Ref 8).	4 μg/l if chloride absent. May be 10 to 100 fold higher if chloride high.	Chloride interferes at about 1.3 μg/l Br^- per 1 mg/l Cl^-	Correction for Chloride interference based on accurate chloride analysis.
4. Gas Chromatography of Cyanogen Bromide formed by reaction with cyanide and chlorine. (Ref 9).	2 μg/l for pure water synthetics usually for higher for natural and treated water samples.	Cadmium, Mercury and Aromatics give low results. Substances with a GC Peak close to CNBr give positive interference. Not reliable in most waters.	
5. Oxidation to Bromate followed by concentration with a silver precipitate followed by polarographic reduction. (Ref 10).	2 μg/l but dependent on carrier concentration step.	Chloride makes resolution of silver precipitates difficult in a form suitable for anode wave polarography.	
6. X-ray Fluorescence spectrophotometry of samples evaporated onto filter paper compared with standards similarly prepared.	This method was not evaluated but is known to be practicable, see Refs 12 and 13.		

Checking the Accuracy of Analytical Results

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate (5). As a minimum, it is recommended that a standard solution of iodide and or iodate of suitable concentration be analysed at the same time and in exactly the same way as normal samples. The results so obtained should be plotted on a quality control chart, which will help determine whether errors are occurring. See also Ref 11.

The same applies for Bromide determinations.

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