The determination of bromate, chlorate and chlorite in waters by ion chromatography 1997

Methods for the Examination of Waters and Associated Materials

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of the materials and apparatus used. The methods in this booklet describe the use of actual materials used, but in no way endorses them as being superior to others. Equivalent materials are acceptable, and it should be understood that the performance characteristics may differ with other materials, and may also vary with different batches. It is left to users to evaluate these procedures in their own laboratories. Performance data are available for the determination of bromate but only limited data are available for chlorate and chlorite.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, groundwater, river and seawater, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests reported for most parameters. These methods should be capable of establishing within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors), systematic error (bias), total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of this publication on whether or not the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets in the series 'Methods for the Examination of Waters and Associated Materials' and their continuous revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

1.0	General principles of sampling and accuracy of results
2.0	Microbiological methods
3.0	Empirical and physical methods
4.0	Metals and metalloids
5.0	General non-metallic substances
6.0	Organic impurities
7.0	Biological monitoring
8.0	Sewage treatment methods and biodegradability
9.0	Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods and the more important parameters and topics is available from HMSO (ISBN 0 11 752669 X).

Every effort is made to avoid errors appearing in the published text. If, however, any are found please notify the Secretary.

Dr D Westwood
Secretary

October 1997

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with The Health and Safety at Work etc Act 1974 and any regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 (SI 1988/1657). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety, and these should be consulted and be readily accessible to all analysts. Amongst such publications are those produced by the Royal Society of Chemistry, namely 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', 5th edition, 1992; by Member Societies of the Microbiological Consultative Committee, 'Guidelines for Microbiological Safety', 1986, Portland Press, Colchester; and by the Public Health Laboratory Service 'Safety Precautions, Notes for Guidance'. Another useful publication is produced by the Department of Health entitled 'Good Laboratory Practice'.

Introduction

For many years, chlorine has been used for the disinfection of drinking waters. However, its use leads to the formation of certain disinfection by-products, in particular, trihalomethanes, which are a significant health concern. Alternative disinfection methods, for example the use of ozone and chlorine dioxide, have therefore been investigated (1) in order to reduce the formation of these by-products.

Ozonation has emerged not only as a promising alternative to chlorination but also as a water treatment chemical for the reduction of pesticide concentrations, and levels of other organic matter which adversely affect the taste and odour characteristics of drinking waters. The use of ozone is, however, not without its own disadvantages. Ozone is a strong oxidant sufficient to cause the oxidation of bromide (which occurs naturally in waters) to bromate. In addition, the presence of bromate has been reported during the on-site electrolytic generation of sodium hypochlorite from brine.

Bromate is a suspected carcinogen and the World Health Organisation (WHO) has recommended a guideline value of 25 μgL^{-1}. Proposals in the revised Drinking Water Directive (2) include a statutory limit of 10 μgL^{-1}.

The level of bromate found in treated waters depends upon the concentration of bromide in the source water, the ozone concentration, the duration of contact and the pH.

The following equations illustrate the pathway by which bromide **(Br^-)** is oxidised (by ozone) to bromate **(BrO_3^-)**, via the intermediate formation of hypobromite **(OBr^-)**.

$$Br^- + O_3 + H_2O \longrightarrow HOBr + O_2 + OH^-$$

$$HOBr + H_2O \longleftrightarrow H_3O^+ + OBr^-$$

$$OBr^- + 2\,O_3 \longrightarrow BrO_3^- + 2\,O_2$$

The equilibrium which is established between hypobromite (OBr^-) and hypobromous acid (HOBr) is pH dependent. Since there appears to be no reaction between ozone and hypobromous acid, and since increased acid concentration will result in increased hypobromous acid, then ozonation at low pH (increased acidity) will tend to minimise bromate formation.

It has been found that the addition of ammonia to hypobromous acid results in the formation of bromamine.

$$HOBr + NH_3 \longrightarrow NH_2Br + H_2O$$

As a consequence of this, the formation of bromate is reduced. Although not a practical consideration, the reaction is useful in that the addition of ethylenediamine or diethylamine can exhibit similar properties and help stabilise samples for bromate analysis. Furthermore, it has been suggested that the addition of a divalent cation, for example calcium or magnesium, aids the recovery of bromate by assisting in the removal of sulphate prior to analysis.

The use of chlorine dioxide, and substances used to generate chlorine dioxide *in situ* is approved by the Secretary of State under regulation 25 of the Water Supply (Water Quality) Regulations 1989 (SI 1989/1147). The use is conditional, provided that the combined concentration (expressed as chlorine dioxide) of chlorine dioxide, chlorite and chlorate in water entering supply does not exceed 500 μgL^{-1}. A similar approval for the use of on-site generation of sodium hypochlorite stipulates that the concentration of chlorate in the treated water must not exceed 700 μgL^{-1}. WHO has proposed a guideline value for chlorite in drinking water of 200 μgL^{-1}.

Chlorite **(ClO_2^-)** and chlorate **(ClO_3^-)** can both be formed as disinfection by-products following the use of chlorine dioxide. The oxyhalide anions are formed as a result of the hydrolysis of chlorine dioxide **(ClO_2)** in water.

$$2\ ClO_2 + 3\ H_2O \longrightarrow ClO_2^- + ClO_3^- + 2\ H_3O^+$$

Chlorate is stable in drinking waters, however, losses of chlorite can be observed within a day. Chlorite reacts with hypochlorite **(ClO^-)** to form chlorate. Chlorite has also been shown to be degraded by UV light.

$$ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^-$$

Existing methods of analysis for the determination of bromate (and to some extent chlorate and chlorite) are predominantly titrimetric and colorimetric in nature. Usually, these techniques lack the sensitivity and selectivity required for individual determinations of these anions at the levels normally found in treated waters. In view of this, the use of ion chromatography would seem a natural choice for the low level analysis of bromate, chlorate and chlorite.

Ion chromatography utilises the ability of ion-exchange resins to separate mixtures of anionic species. A suitable liquid eluent is used to transport the sample through the system. After elution from the column, the individual anions are detected, for example using chemically suppressed conductivity, and quantified. For a more detailed description refer to "The determination of anions and cations, transition metals, other complex ions and organic acids and bases by chromatography 1990" in this series.

Methods using ion chromatography are described within this booklet for the determination of bromate (employing pre-concentration) and chlorate and chlorite (by direct injection). The use of capillary electrophoresis is referred to later in the booklet. Capillary electrophoresis is a developing technique but appears to be presently viable for the determination of bromate, chlorate and chlorite only at higher concentrations.

Techniques involving flow injection analysis with colorimetric determination are being developed and have been reported.

A The Determination of Bromate in Waters

A1 Performance characteristics of the method

A1.1	Substance determined	Bromate. Other anions may also be determined, for example chlorate and chlorite.
A1.2	Type of sample	Drinking waters, raw waters and partially treated waters.
A1.3	Basis of method	The sample is treated with barium and silver cationic resins to reduce interferences due to sulphate and chloride respectively. The treated sample is "cleaned-up", concentrated on-column and is then ready for determination by ion chromatography (IC) using chemically suppressed conductivity detection.
A1.4	Range of application	Up to 100 μgL^{-1} - the upper limit may be extended by dilution of the sample.
A1.5	Calibration curve	The method is linear over the range of application.
A1.6	Standard deviation	See Table A1.
A1.7	Limit of detection	Typically 0.5 μgL^{-1}. See Table A1.
A1.8	Sensitivity	On a range of 1 µS, a 10 μgL^{-1} standard bromate solution should produce a response between 0.2 - 0.25 µS.
A1.9	Bias	See Table A1.
A1.10	Interferences	No direct interferences are known; however, any determinand which has a similar chromatographic retention time to bromate and which gives a detector response will interfere. Chromatographic problems will arise if chloride levels are above 1-2 mgL^{-1}. Carbonate interferences are known to occur, especially when high concentrations of sodium hydroxide are used.
A1.11	Time required for analysis	The overall analysis time is approximately 30 minutes per sample.

A2 Principle

The sample is first pre-treated to reduce levels of chloride, other halides and sulphate. Separate cartridges containing silver (for halide removal) and barium (for sulphate removal) are used. The cartridges contain cationic exchange resins which reduce the concentration of interfering anions by the formation of insoluble precipitates. The pre-treatment is necessary in order to prevent overloading of the anionic concentrator column during the subsequent concentration stage; it also minimises chromatographic interference of chloride.

The pre-treated sample is then concentrated by passing a known volume through a concentrator column. A pump (using water as eluent) is used to transfer the sample from a loop, through a clean-up column on to the concentrator column. The clean-up column is required because the pre-treatment causes residual silver and barium to be present in the sample. Silver and barium bind to the resin material in the concentrator and analytical columns, resulting in a loss of performance.

The concentrated sample is then eluted through an analytical column using a borate eluent. Alternatively, a sodium hydrogencarbonate eluent can be used. A schematic representation is shown in Figure A1 and a typical chromatogram is shown in Figure A2.

After the elution of bromate and remaining chloride, the column is purged with a strong borate solution (or sodium carbonate and sodium hydrogencarbonate solution) to remove highly retained ions such as nitrate, phosphate and traces of sulphate.

The determination is carried out using chemically suppressed conductivity detection.

A3 Apparatus

Volumetric glassware should be of grade B (or better).

A typical system consists of the following items in series (see also Figure A1):

A3.1 Eluent reservoir and degas unit for two eluents.

A3.2 Inert eluent pump capable of producing a flow of 2 $mLmin^{-1}$ and performing step gradient or eluent switching.

A3.3 A six-way injector fitted with a 3 mL loop.

A3.4 Sample pump set at 2 $mLmin^{-1}$ used to transport the pre-treated sample to the concentrator column.

A3.5 Clean-up column.

A3.6 A four-way valve fitted with an anionic guard/concentrator column.

A3.7 Anionic separator/analytical column.

A3.8 If applicable, an anionic self-regenerating or micromembrane suppressor may be used; the latter requires a regenerant flow rate of approximately 5 to 10 $mLmin^{-1}$.

A3.9 Conductivity detector capable of measuring down to 1 µS output range.

A3.10 If applicable, a device for timing and controlling valve and pump actions.

A3.11 Recording or data handling device.

Pre-treatment cartridges containing the cationic exchange resins are commercially available.

A4 Hazards

Concentrated solutions of nitric acid and sulphuric acid are corrosive. Appropriate safety procedures should be followed. Bromate is a suspected carcinogen.

A5 Reagents

Reagents of recognised analytical grade should be used unless otherwise stated.

A5.1 **Water**. To maintain performance and extend column lifetime, water should be deionised, have a resistivity greater than 18 megohm/cm and should not contain particles larger than 0.20 µm.

A5.2 **Regenerant solution.** If a micromembrane suppressor is used then a solution of sulphuric acid is required. Cautiously add 2.8 ± 0.1 mL of concentrated sulphuric acid (d_{20} 1.84) to 4 litres of water (A5.1). Mix well.

A5.3 **Standard stock solution - 1000 mgL^{-1}**. Solids used to prepare standard solutions should be dried for one hour at 105 °C and stored in a desiccator. Stock solutions should be stored in amber bottles and kept in the dark at 4°C. Stock solutions are stable for at least one month when stored correctly.

Prepare a stock solution of bromate at a concentration of 1000 mgL^{-1} (as bromate) by dissolving 1.306 ± 0.001 g of potassium bromate in water (A5.1) in a 1000 mL volumetric flask. Make up to the mark with water (A5.1) and mix well.

Prepare at least five standard calibration solutions covering the expected range, for example up to 20 μgL^{-1}. Add accurately measured volumes of the standard stock solution to separate volumetric flasks and dilute to volume with water (A5.1). One of the standard solutions should be a blank. The lowest standard calibration solution should contain bromate at a concentration slightly greater than the expected limit of detection. The highest standard calibration solution should be greater than the highest expected concentration of bromate in the sample. Prepare the solutions freshly for each day of measurement.

If, in order to increase the analytical range, a second sensitivity scale on the detector is used, then both sensitivity levels should undergo calibration using the standard solutions.

A5.4 Eluents.

A5.4.1 Dissolve 15.255 ± 0.01 g of sodium borate ($Na_2B_4O_7.10H_2O$) in approximately 950 mL of water (A5.1). Make up to a volume of 1 litre with water (A5.1) and mix well.

A5.4.2 Dissolve 95.343 ± 0.01 g of sodium borate ($Na_2B_4O_7.10H_2O$) in approximately 950 mL of water (A5.1). Make up to a volume of 1 litre with water (A5.1) and mix well.

The water used to make up the eluents should be degassed with helium (A5.5) for 5 minutes prior to addition of the above reagents. Both reagents should be added to the degassed water in the degas unit to prevent carbon dioxide absorption.

Alternatively, eluent A5.4.1 can be replaced with sodium hydrogencarbonate; dissolve 0.672 ± 0.01 g sodium hydrogencarbonate ($NaHCO_3$) in approximately 950 mL of water (A5.1). Make up to a volume of 1 litre with water (A5.1) and mix well. Eluent A5.4.2 can be replaced with a mixture of sodium carbonate and sodium hydrogencarbonate; dissolve 0.424 ± 0.01 g sodium carbonate (Na_2CO_3) and 0.126 ± 0.01 g sodium hydrogencarbonate in approximately 950 mL of water (A5.1). Make up to a volume of 1 litre with water (A5.1) and mix well.

A5.5 Helium.

A5.6 Nitric acid 0.1M.

A6 Sample collection and preservation

Samples should be collected in clean, amber coloured glass or polyethylene bottles and stored at 4°C. Limited stability data (3) for raw and treated waters have indicated that samples with bromate concentrations around 10 μgL^{-1} are stable for up to approximately 2 months. However, it has been reported (4) that the addition of ethylenediamine reduces further formation of bromate once the sample has been taken.

A7 Analytical procedure

Step	Procedure	Notes
Sample pre-treatment		
A7.1	Prepare barium and silver cartridges either according to manufacturer's instructions or as required (note a).	(a) Samples and standard solutions require a clean-up stage in order to prevent overloading of the anionic concentrator column and to reduce interferences.
A7.2	Pass approximately 8 mL of sample, filtered if necessary, through the barium cartridge. Discard the first 1 mL and collect the remainder (note b).	(b) The flow rate through each cartridge is critical to ensure maximum efficiency of chloride (and sulphate) removal. The flow rate should be constant and not too fast.
A7.3	Pass the remaining sample, approximately 7 mL, through the silver cartridge (note b). Discard the first 2mL and use the remainder for analysis (note c).	(c) The use of one cartridge per sample will ensure maximum ion removal efficiency. Whilst samples are being chromatographed, other samples can be prepared by passing them through the cationic cartridges.
Ion chromatography		
A7.4	Using eluent A5.4.1, start the ion chromatograph in accordance with manufacturer's instructions (note d).	(d) The instrument is ready as soon as the baseline is stable at the 1 µS output range.
A7.5	The pre-treated sample, standard or blank solution is loaded into a loop using a syringe or autosampler (note e).	(e) The loop should not be too large (for example not greater than 3 mL) otherwise the concentrator column may be overloaded.
A7.6	The six-way valve is switched into position, in sequence, to allow passage of the sample, standard and blank solutions through the clean-up column and onto the concentrator column. Water is used as carrier (note f).	(f) The clean-up column contains a chelating resin which should be cleaned regularly with 0.1M nitric acid to remove final traces of heavy metals, including silver.
A7.7	After sufficient time has elapsed to allow all the contents of the sample loop to be flushed on to the concentrator column, the four-way valve is switched into position. Eluent A5.4.1 transports the concentrated ion solution on to the analytical column.	
A7.8	After approximately 6 minutes (ie after chloride has been eluted) eluent A5.4.2 is introduced into the system and maintained for at least 5 minutes (note g).	(g) These times are approximate and should be determined by experiment. All valve and pump operations can be externally controlled by a time-sequencing device.
A7.9	Switch back to eluent A5.4.1 for at least 7 minutes for equilibration to occur.	

A8 Calibration and quantification

Each of the calibration standard solutions should be treated in the same way as samples. Peak areas or heights should be determined and a calibration graph constructed. Bromate can be identified in the sample by comparing the retention time with those of standard bromate solutions. This should be confirmed by spiking samples with added bromate. Concentrations may be read off against the calibration graph, or more conveniently, an integrator or PC-based data handling system can be used.

A9 Blanks, recoveries and AQC

Adequate blank values should be obtained using interference-free water before samples are determined. At least one reagent blank should be analysed with each batch of samples. Check the efficiency of the analytical procedure by adding suitable amounts of bromate to samples. Carry out the entire procedure using water of a similar nature to the sample being analysed spiked with bromate at appropriate concentrations.

The results in Table A1 show that in one laboratory poor recoveries were obtained on real samples. To address this problem it is essential that AQC solutions contain samples with and without spiked additions of bromate in order to confirm the identification of bromate in the chromatographic determination.

Table A1 Means, standard deviations, recoveries and limits of detection

	Mean	St	Recovery %	LOD
Laboratory 1				
2 μgL^{-1} standard	2.394	0.429		1.48
10 μgL^{-1} standard	9.926	1.248		
sample	0.949	0.615		
sample spiked with 10 μgL^{-1}	3.103	1.005	21.5	
Laboratory 2				
2 μgL^{-1} standard	1.750	0.185		0.30
10 μgL^{-1} standard	9.898	0.407		
sample	2.637	1.051		
sample spiked with 10 μgL^{-1}	12.79	1.876	101.57	
Laboratory 3				
2 μgL^{-1} standard	2.032	0.240		0.46
10 μgL^{-1} standard	9.899	0.354		
sample	2.610	0.967		
sample spiked with 10 μgL^{-1}	12.43	0.707	98.22	

All units expressed in μgL^{-1} unless otherwise indicated.
St is total standard deviation.
LOD is limit of detection (calculated as 4.65 x within-batch standard deviation).
Sample consisted of a treated water.
All results are based on 11 batches analysed in duplicate.
The column used was a Dionex AS9-SC column.

Note: Laboratory 1 did not use the eluents referred to in section A5.4. This laboratory used high purity water as the first eluent and a sodium hydroxide - boric acid solution as the second eluent. It is not known whether matrix interference effects were involved, and why poor results were obtained when real samples were analysed. Standard solutions were satisfactory.

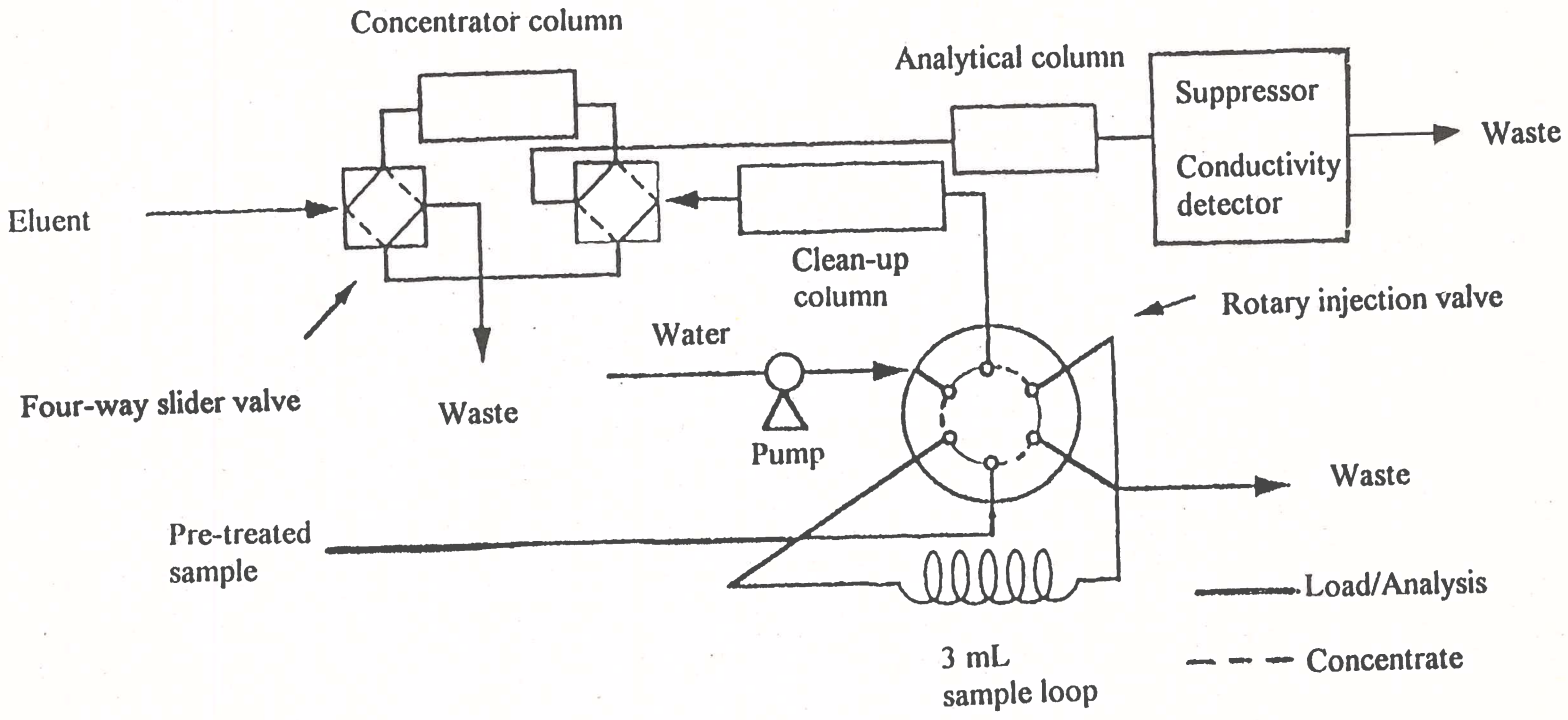


Figure A1 Schematic instrumentation for bromate determination (pre-concentration)

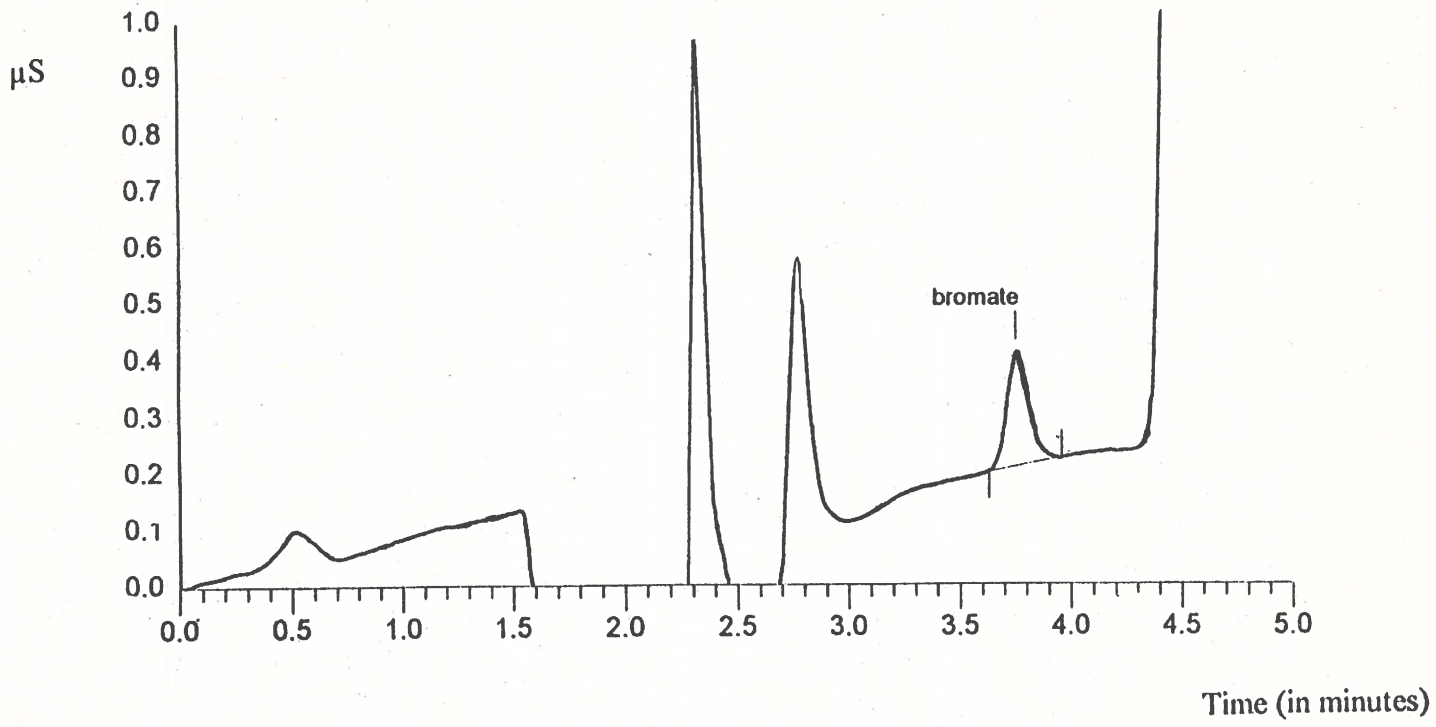


Figure A2 Ion chromatogram of bromate (pre-concentration)

B The Determination of Chlorate and Chlorite in Waters

B1 Performance characteristics of the method

B1.1	Substance determined	Chlorate and chlorite. Other ions may also be determined, for example bromide.
B1.2	Type of sample	Drinking waters, raw waters and partially treated waters.
B1.3	Basis of method	Direct injection by ion chromatography (IC) using chemically suppressed conductivity detection.
B1.4	Range of application	Up to 1000 μgL^{-1}. The range may be extended by dilution of the sample.
B1.5	Calibration curve	The method is linear over the range of application.
B1.6	Standard deviation	See Table B1.
B1.7	Limit of detection	Typically 10 μgL^{-1} for chlorate and chlorite, and 40 μgL^{-1} for bromide. See Table B2.
B1.8	Bias	See Table B1.
B1.9	Interferences	No direct interferences are known; however, any determinand which has a similar chromatographic retention time and which gives a detector response will interfere. Nitrate elutes very close to chlorate.
B1.10	Time required for analysis	Approximately 15 minutes per sample.

B2 Principle

No pre-treatment of the sample is usually necessary and the sample is directly injected into an ion chromatography system using suppressed conductivity detection.

B3 Apparatus

A typical ion chromatographic system similar to the one depicted in Figure A1 is required.

B3.1 Eluent reservoir and degas unit for one eluent.

B3.2 Inert eluent pump capable of producing a flow of 2 $mLmin^{-1}$.

B3.3 A six-way injector fitted with a 50 µL loop.

B3.4 Anionic guard column.

B3.5 Anionic separator/analytical column.

B3.6 If applicable, an anionic self-regenerating or micromembrane suppressor may be used; the latter requires a regenerant flow rate of approximately 5 to 10 $mLmin^{-1}$.

B3.7 Conductivity detector capable of measuring down to 1 µS output range.

B3.8 If applicable, a device for timing and controlling valve and pump actions.

B3.9 Recording or data handling device.

B4 Hazards

Concentrated sulphuric acid is corrosive. Appropriate safety procedures should be followed.

B5 Reagents

Reagents of recognised analytical grade should be used unless otherwise stated.

B5.1 **Water.** To maintain performance and extend column lifetime, water should be deionised, have a resistivity greater than 18 megohm/cm and should not contain particles larger than 0.20 µm.

B5.2 **Regenerant solution.** If a micromembrane suppressor is used then a solution of sulphuric acid is required. Cautiously add 2.8 ± 0.1 mL of concentrated sulphuric acid (d_{20} 1.84) to 4 litres of water (B5.1) and mix well.

B5.3 **Standard stock solutions** - 1000 mgL^{-1}. Solids used to prepare standard solutions should be dried for one hour at 105 °C and stored in a desiccator. Stock solutions should be stored in amber bottles and kept in the dark at 4°C. Stock solutions are stable for at least one month when stored correctly.

B5.3.1 Chlorate stock solution. Dissolve 1.467 ± 0.001 g potassium chlorate in approximately 900 mL of water (B5.1) in a 1 litre volumetric flask. Make up to the mark with water and mix well.

B5.3.2 Chlorite stock solution. Dissolve 1.341 ± 0.001 g sodium chlorite in approximately 900 mL of water (B5.1) in a 1 litre volumetric flask. Make up to the mark with water and mix well.

B5.3.3 Bromide stock solution. Dissolve 1.489 ± 0.001 g potassium bromide in approximately 900 mL of water (B5.1) in a 1 litre volumetric flask. Make up to the mark with water and mix well.

B5.3.4 Mixed stock solution - 10 mgL^{-1}. Pipette 10.00 ± 0.02 mL of each of the stock solutions (B5.3.1 - B5.3.3) into a clean 1 litre volumetric flask. Dilute to the mark with water (B5.1) and mix well. This solution is stable for up to 1 week if stored correctly in the dark at 4°C.

B5.3.5 Mixed calibration standard solutions. Into a series of 100 mL volumetric flasks, pipette for example 1, 3, 7 and 10 mL aliquots of the mixed stock solution (B5.3.4). Dilute to the mark with water (B5.1) and mix well. The calibration solutions should be made fresh on the day the analysis is carried out. The above solutions represent concentrations in the range 100 - 1000 μgL^{-1}. A blank solution should also be prepared. The lowest calibration concentration should not greatly exceed the expected limit of detection.

B5.4 **Eluents.**

B5.4.1 Dissolve 7.416 ± 0.001 g analytical reagent grade orthoboric acid and 1.5 ± 0.05 mL analytical reagent grade 46-48 % sodium hydroxide solution in 950 mL of water (B5.1) in a 1 litre volumetric flask. Make up to the mark with water and mix well. Degas.

B5.4.2 Dissolve 14.83 ± 0.01 g analytical grade reagent orthoboric acid in approximately 950 mL of water (B5.1) in a 1 litre volumetric flask. Add 3.00 ± 0.05 g analytical grade reagent 46-48% sodium hydroxide solution. Make up to the volume with water (B5.1) and mix well. Degas.

B6 Sample collection and preservation

Samples should be collected in clean, amber coloured glass or polyethylene containers and stored at 4°C. Samples should be analysed as soon as possible after collection.

B7 Analytical procedure

Step	Procedure	Notes
Sample pre-treatment		
B7.1	If samples contain suspended material, filter through a 0.2 µm filter.	
Ion chromatography		
B7.2	Set up the ion chromatograph in accordance with the manufacturer's instructions and allow to equilibrate (note a).	(a) The instrument is ready for use when the baseline is stable at the 0-1 µS range.
B7.3	The sample, standard or blank solution is loaded into the injection loop using a syringe or auto-sampler. The injection valve is switched to transfer the solution onto the column. When all peaks have eluted, the system is ready for the next injection (note b).	(b) The run time is approximately 12 minutes and sulphate is normally the last ion to elute. The retention time may be checked by running a separate sulphate solution. Alternatively, the system can be purged with eluent B5.4.2 when chlorite and chlorate have eluted. If so, switch back to eluent B5.4.1 after purging and allow to equilibrate.

B8 Calibration and quantification

Each of the calibration standard solutions should be treated in the same way as samples. Peak areas or heights should be determined and a calibration graph constructed. Ions can be identified in the sample by comparing retention times with those of individual standard solutions. This should be confirmed by spiking samples with an appropriate concentration of anion and the spiked sample re-analysed. Concentrations may be read off against the calibration graph, or, more conveniently, an integrator or PC-based data handling system can be used.

B9 Blanks, recoveries and AQC

Adequate blank values should be obtained using interference-free water before samples are determined. At least one reagent blank should be analysed with each batch of samples. Check the efficiency of the analytical procedure by adding suitable amounts of standard solutions to samples. Carry out the entire procedure using water of a similar nature to the sample being analysed spiked with appropriate anions of suitable concentration.

Table B1 Means and standard deviations

	Mean	St	Sw
Chlorite *			
Tap water spiked with 250 μgL^{-1}	254.24	7.0	3.4
Tap water spiked with 750 μgL^{-1}	761.54	33.2	
Chlorate #			
Tap water spiked with 250 μgL^{-1}	231.58	19.8	12.3
Tap water spiked with 750 μgL^{-1}	743.17	25.2	

All units expressed in μgL^{-1}.
Five batches were each analysed five times.
St is total standard deviation.
Sw is within-batch standard deviation.
* uncorrected results.
# blank corrected results.
Data taken from reference 5.

Table B2 Standard deviations and limits of detection

	St	Limit of detection
Chlorite		
Deionised water	2.2	10
Water	1.5	7
Chlorate		
Deionised water	4.7	21
Water	1.6	7

All units expressed in μgL^{-1}.
Ten spiked solutions each containing 50 μgL^{-1} were analysed.
Water comprised 2 mgL^{-1} of fluoride, 250 μgL^{-1} of bromide, 60 mgL^{-1} of nitrate, 160 mgL^{-1} of sulphate.
Data taken from reference 5.

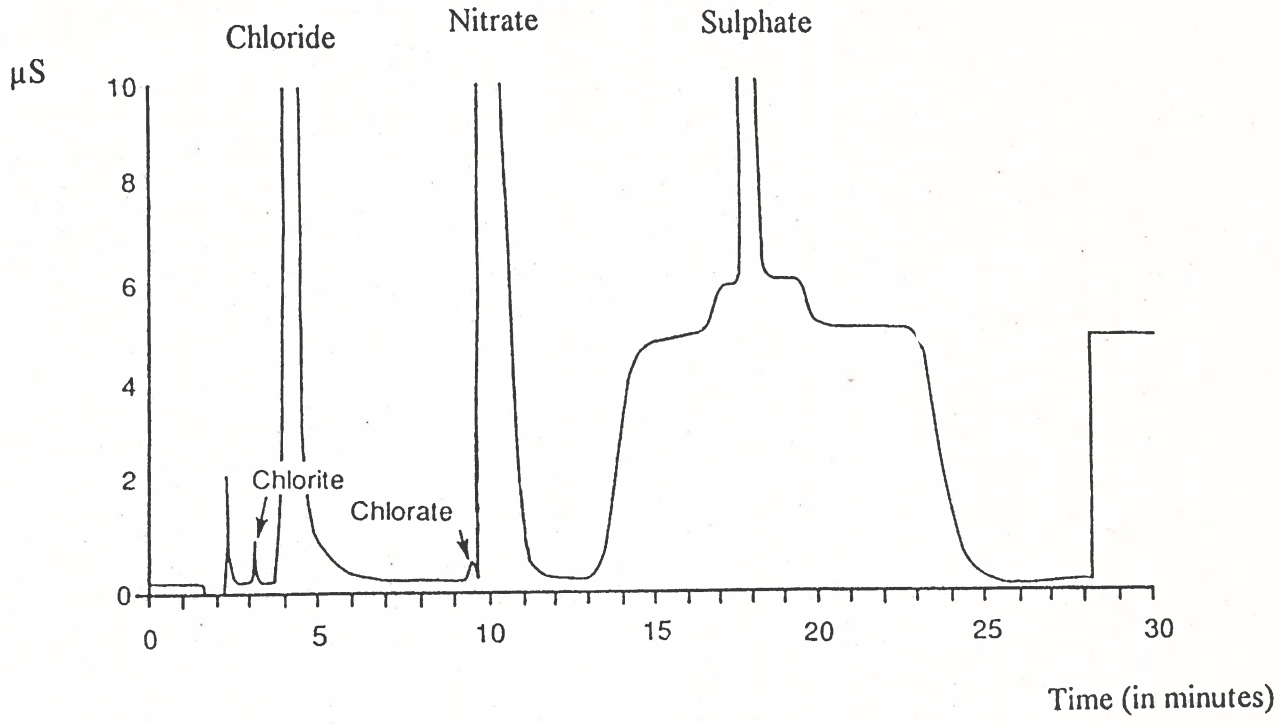


Figure B1 Ion chromatogram of tap water spiked with chlorate and chlorite at 250 μgL^{-1}

C Capillary Electrophoresis

Instruments for capillary electrophoretic determinations first became commercially available in 1989. The technique is similar to liquid chromatography and is capable of achieving fast and efficient separation of a wide range of polar and non-polar compounds. Initially, the technique was used for the separation of biological ions, such as proteins, peptides and drugs. More recently, the technique has been used for analysing environmental samples and in particular for inorganic ions.

In its most common form, ie free-zone electrophoresis, a small volume of sample is placed at one end of a capillary column (usually made of silica with an internal diameter of approximately 10-100 μm). The capillary column is filled with an appropriate buffer. Under the influence of a high voltage (normally 10 to 30 kilovolts) ions separate according to their charge to mass ratio. At the same time, these ions are transported towards a detector via electro-osmotic flow. The most commonly used detector is an ultraviolet (UV) detector, and the capillary column itself acts as the flow cell. See Figure C1 for a schematic diagram.

The technique has been applied to the separation of inorganic anions, cations and organic acids with detection by indirect UV. Oxyhalides can also be separated (see Figure C2). Because the concentration sensitivity for capillary electrophoresis is approximately an order of magnitude less than that normally available for ion chromatography, the technique appears not to be presently suitable for the determination of bromate, chlorate and chlorite at the concentrations normally encountered in drinking water.

In many cases, capillary electrophoresis offers a fast and efficient alternative technique to high performance liquid chromatography and ion chromatography. Rapid advances are in progress and improvements in column and detection technology may offer greater scope and acceptance of the technique for routine applications.

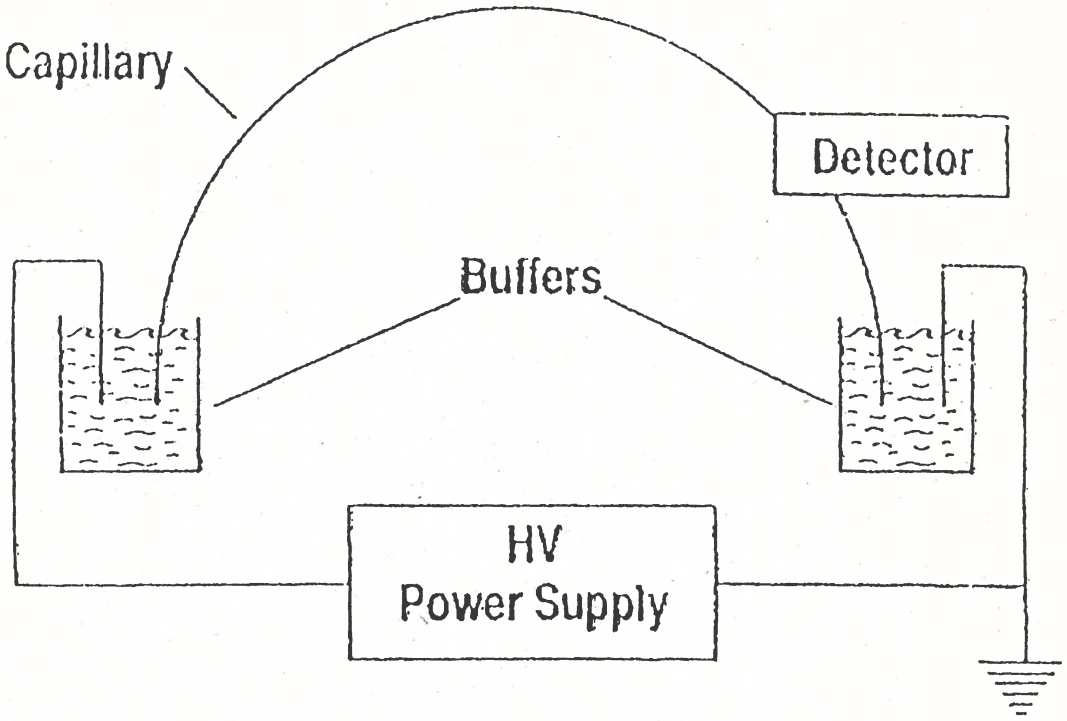
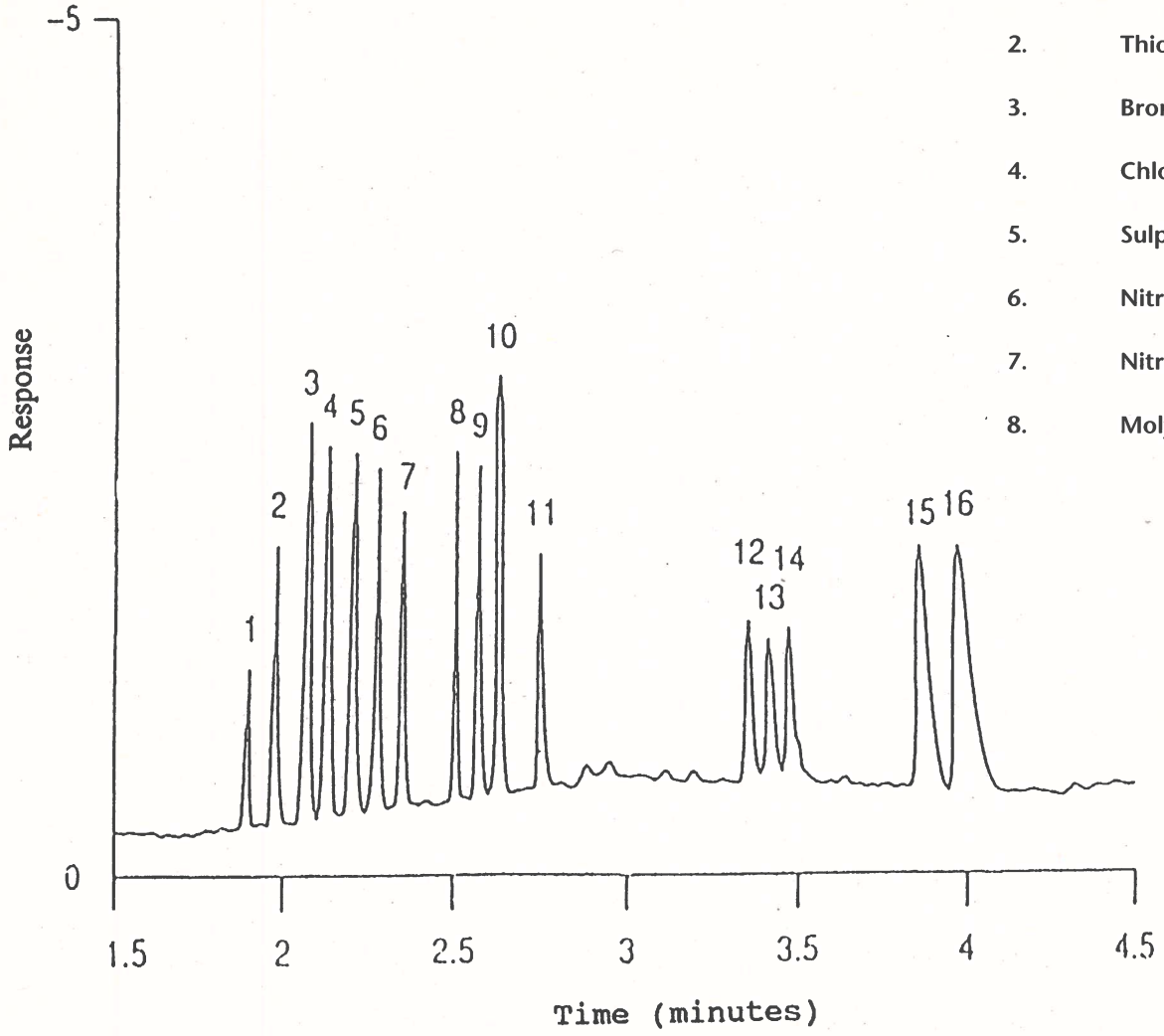


Figure C1 Capillary electrophoresis - basic schematic representation



Peak:

1.	Dithionate	9.	Azide
2.	Thiosulphate	10.	Thiocyanate
3.	Bromide	11.	Chlorate
4.	Chloride	12.	Fluoride
5.	Sulphate	13.	Bromate
6.	Nitrite	14.	Formate
7.	Nitrate	15.	Phosphate
8.	Molybdate	16.	Phthalate

Figure C2 Typical capillary electrophoresis chromatogram

References

1. Disinfection By-Products. Proceedings of a Drinking Water Inspectorate Seminar held at Medmenham, 2-3 February 1993. Edited by J Hutchison.

2. Commission of the European Communities. COM(94) 612 final. 95/0010 (SYN). Proposal for a Council Directive concerning the quality of water intended for human consumption.

3. Bromate in treated waters: Supervision of performance tests. Report to the Department of the Environment, July 1995, DWI/3880/1, PECD EPG/1/9/48.

4. Detecting bromate with IC. WWT January 1995, pp15.

5. The determination of chlorate and chlorite in drinking water, July 1993, FWR Report FR0390.

Analytical Quality Control

1 Routine control

Once a method has been selected for routine use, a system of analytical quality control should be adopted in order to validate the analysis. At least one control standard should be analysed with each batch of samples and the results plotted on a control chart. Corrective action should be taken if one value falls outside of the action limit (at ± 3s) or two consecutive values exceed the warning limit (at ± 2s). As more data are acquired, the standard deviation, s, should be updated and the control chart limits recalculated.

2 Estimation of the accuracy of analytical results using these methods

None of the methods given in this booklet has been thoroughly investigated for all types of samples and before general use the accuracy achievable should be known. It would be of great value if any laboratory using or considering the use of any of these methods would estimate the accuracy of its own analytical results and report the findings to the Secretary of the Standing Committee of Analysts.

Address for correspondence

However well a method is tested, there is always the possibility of discovering a hitherto unknown problem. Users with information on these methods are requested to write to the address below:

The Secretary
The Standing Committee of Analysts
Environment Agency
Steel House
11 Tothill Street
London
SW1H 9NF

Environment Agency

Standing Committee of Analysts

Members assisting with these methods

M Clay
R Cochrane
J Dunning
J Gale
T Newby
G Small
A Stagg

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