Spectrophotometric determination of low levels of bromate in drinking water after reaction with fuchsin

L. Romele, and M. Achilli*

CISE SpA, Via Reggio Emilia 39, Milan, 20090 Segrate, Italy. E-mail: 0909ACHI@s1.cise.it

A simple spectrophotometric procedure for the determination of trace levels of bromate in drinking water is described, which uses metabisulfite reduction to form bromine and reaction with reduced fuchsin to form a bromurated red coloured product absorbing at 530 nm. The present procedure is free of known interferences (Cl^-, ClO_3^-, SO_4^{2-}) which affect other commonly used analytical techniques, such as ion chromatography, and thus require time consuming steps for separation with additional costs. Cationic interferences from heavy metals and major elements are removed by passage through a strong cationic resin (Na^+ form). The sample is then mixed with a little volume of fuchsin solution decoloured with excess of metabisulfite in HCl medium and 1–2 ml of citrate buffer solution (pH 3.4). Bromate is converted to bromine by metabisulfite and subsequently reacts with fuchsin regenerating the quinoide structure absorbing at 530 nm. Maximum colour development occurs at about 26 min after reagent addition and absorbance is stable for at least 30 min. The response is linear up to 20 μg l^{-1} of bromate. The detection limit (propagation of errors approach) is 1 μg l^{-1} (40 mm path length) and the precision (short term relative standard deviation) is 6% at 5 μg l^{-1} level of bromate (n = 10). This method allows a low detection limit to be reached making it particularly attractive for accurate control of bromate level in drinking water in accordance to the European standard.

Keywords: *Bromate determination; spectrophotometry; trace concentration; drinking water; fuchsin*

Bromate in drinking water is a disinfection byproduct (DPB) of the ozonation of bromide containing waters[1].

Bromide concentration in raw waters for drinking water production varies from a few μg l^{-1} up to several mg l^{-1}.[1] The major sources of bromide in inland waters are related to local geological situations, natural fractionation and anthropogenic bromide emissions, such as from soda production, potassium and coal mining.

The common level of bromate in drinking water ranges from 3 to 8 μg l^{-1},[2] with extreme cases of about 0.05 μg l^{-1} and more than 30 μg l^{-1}.[3] The level of bromate in ozonated drinking water depends upon many factors[2] including the natural level of bromide present in the source water and the ozone dose. For initial bromide concentration from 35 to 50 μg l^{-1} and 1 mg l^{-1} ozone dose (high exposure) the bromate concentration comes close or even exceeds the value of 25 μg l^{-1} for bromate proposed as a guideline by the World Health Organization (WHO).[4] Increasing dosage leads to high percentage increase (50%) in bromate formation.[5]

Bromate has been known as a possible carcinogen since 1990[5] and for this reason has been considered for regulation by the EPA (Environmental Protection Agency) as a part of a DBP rule. The previous established maximum value of 25 μg l^{-1} was reduced to 10 μg l^{-1} following the increased suspicion of its carcinogenicity. The same value was proposed by the Drinking Water Commission of the European Union.[6]. Recently WHO has proposed a guideline of < 0.5 μg l^{-1} bromate.[2]

Determination of bromate at ppb levels requires a sensitive and accurate method with a low ppb detection limit. Liquid chromatography has been successfully applied to drinking water analysis but it suffers from the existence of interferences which require time consuming steps for elimination, clean-up and separation before the instrumental measurements. When ion chromatography is applied to bromate analysis, matrix problems are often experienced in resolving low levels of bromate from typical background levels of chloride,[7] even using the weak eluent sodium hydroxide–boric acid. Chloride is removed[2] by clean-up on a cationic resin cartridge in silver form, which also removes bromide. A second clean-up step with a cationic resin in hydrogen form is applied to remove residual silver ions. Finally a clean-up with a resin in Ba^{2+} form is used to reduce the level of sulfate in the sample, which can interfere in the chromatographic determination by acting as an eluent causing displacement of bromate. The detection limit using this procedure is about 7 μg l^{-1}.[7,8] Von Gunten and Hoigné[1] reported detection limits in the range 5–25 μg l^{-1} depending on chloride concentration.

The major drawback of these methods is that the amount of bromate in a typical ozonated water sample is near or below the current detection limits; thus a preconcentration step is needed as described by several authors.[2,5,8,9] The performance of the concentration step can be seriously limited by column capacity and ion exchange competition: pre-separation of background anions (*e.g.*, chloride and sulfate) is mandatory. Organic impurities can also affect the performances of the chromatographic system.[9]

A weaker borate eluent can be used to improve separation, but in this case a longer analytical time is required because a second step with a stronger eluent is needed to purge the column before the next injection.[5] With the preconcentration ion chromatographic method a detection limit of 1 μg l^{-1} is achieved for bromate analysis in drinking water.

Jain *et al.*[10] reported a method for the determination of bromate by HPLC after removal of any free bromide and reduction of bromate to bromide. The method involves a precolumn derivatization of bromide to 4-bromoacetanilide by reaction with 2-iodobenzoic acid and acetanilide and sample clean-up by solid phase extraction on C_{18} cartridge. A detection limit of 2.5 μg l^{-1} is obtained.

In this paper a simple and sensitive spectrophometric method is described for bromate analysis in drinking water, which overcomes most of the difficulties encountered using other procedures. A very low detection limit is obtained and potential interferences are easily reduced or eliminated. Work is in progress for the automation of the procedure by using a flow injection system: the results will be reported in another paper.

Experimental

Apparatus

A Pye Unicam Model SP9 UV/VIS spectrophotometer (Cambridge, UK) was used for the experimental work, both in the

fixed and scanning wavelength mode, with 2 mm spectral bandwidth. A 40 mm optical path glass cell was used for all the measurements.

Reagents and standard solutions

All glassware must be thoroughly cleaned before use by soaking in 1.2 M HCl, treating in ultrasonic bath for 15 min and finally rinsing with deionized water. The glass measuring cell was stored in water after measurement.

The fuchsin colour developing reagent was prepared by dissolving 100 mg of basic fuchsin ($C_{19}H_{18}N_3Cl$, Carlo Erba, Milan, Italy) in 100 ml of deionized water in a glass flask. A 10 ml volume of this solution was then added to 0.5 ml of 6 M HCl, followed by 200 mg of sodium metabisulfite (Carlo Erba). The solution was made up to 100 ml with water in a glass flask and left to stand overnight for complete decolouration. The addition of metabisulfite in acidic medium causes the distruction of the quinoide structure of fuchsin thus making the original red colour disappear. The optimum metabisulfite/fuchsin molar ratio was studied in detail (see Results and discussion) in terms of maximum response and signal stability. This solution is stable for 1 month, if stored in glass bottle, at room temperature and protected from light.

The citrate buffer solution (pH 3.4) was prepared by dissolving 44.84 g of citric acid (Carlo Erba) and 11.28 g of NaOH pellets (Carlo Erba) in 500 ml of deionized water. A 45.4 ml volume of this solution was mixed with 54.6 ml of 1 M HCl. The final pH was 3.4.

Bromate standard solutions were obtained by dilution of a 1000 mg l^{-1} concentrated stock solution prepared by dissolving the appropriate amount of solid $KBrO_3$ (Carlo Erba, assay > 99.0%) in deionized water.

Sodium and potassium salts of different anions and heavy metal compounds (Carlo Erba) were used for interference studies after dilution to the desired concentration.

Procedure

On the basis of the optimization experiments, the following procedure was adopted. The standard solutions for bromate analysis in drinking water were prepared in deionized water.

Standard solutions for calibration were prepared by adding 1.25 ml of citrate buffer solution and 0.2 ml of colour developing reagent to a final volume of 25 ml. After homogenization the solutions were left to stand for 30 min for complete and stable colour development. The absorbance was final recorded at 530 nm using a 40 mm cell, against an air reference.

Drinking water samples were passed through a column (30 × 15 mm) of strong cationic resin (Dowex 50), converted to the Na^+ form by treatment with saturated NaCl solution. Before use the resin was washed with deionized water. The first 3 ml of sample eluted from the column were discarded and then 25 ml of sample were added with 1.5 ml of 0.1 M HCl, 1.25 ml of citrate buffer solution and 0.2 ml of colour reagent (final pH: 3). After 30 min the absorbance was measured at 530 nm. Some blank samples in deionized water were treated in the same manner but without passing through the cationic resin. Colorimetric reaction was best performed in a controlled temperature environment (about 20 °C).

Results and discussion

Preparation of colour developing reagent

the fuchsin–bromate solution has a strong maximum absorbance at 530 nm, as shown in the spectra reported in Fig. 1. The experimental tests showed a dependence of the maximum achievable response for bromate on metabisulfite/fuchsin molar ratio. In Fig. 2 this dependence is clearly depicted, together with the behaviour of the signal of the blank. The net absorbance significantly increases from a ratio of 17 to a ratio of 34, decreasing afterwards. A metabisulfite/fuchsin molar ratio of 34 was then selected for further experimental work.

Colour reagent volume

The absorbance response at fixed bromate concentration is dependent upon the volume of colour developing reagent added. For a 25 ml sample or standard solution volume (concentration range 1–20 μg l^{-1}) the absorbance does not vary from 0.2 to 0.5 ml of added reagent, but it decreases abruptly at 2 and 4 ml reagent addition, when blank solution and sample show almost the same aborbance values (Fig. 3). Therefore, 0.2 ml of colour

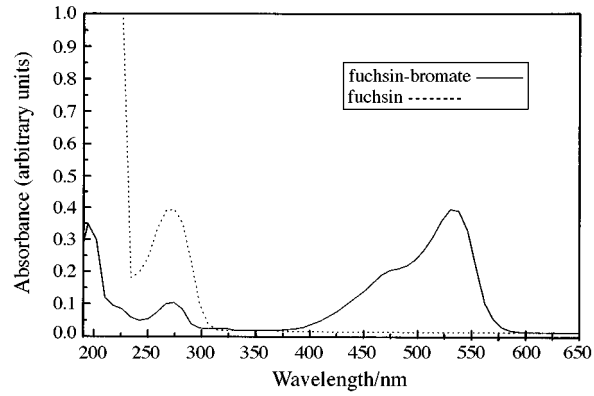

Fig. 1 Spectrum of fuchsin and fuchsin–bromate complex in the range 190–650 nm (20 nm cm^{-1}; span = 1; cell: 10 mm).

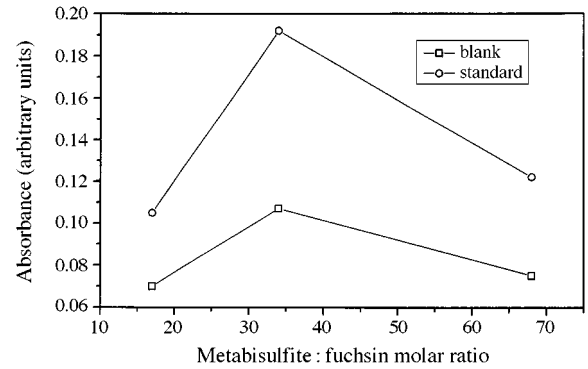

Fig. 2 Effect of metabisulfite–fuchsin molar ratio on absorbance readings at 530 nm for a bromate standard solution (10 μg l^{-1}) and blank at fixed operating conditions (40 mm cell)

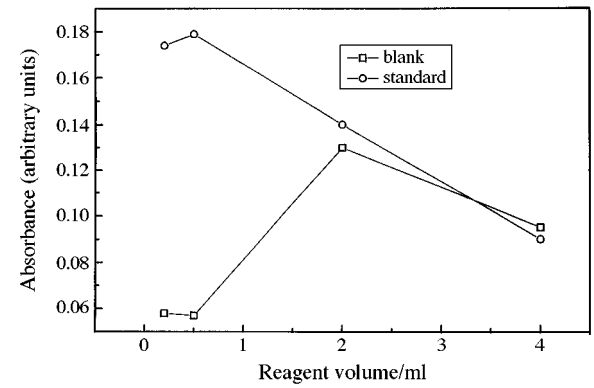

Fig. 3 Effect of colour reagent volume on absorbance readings for a the fuchsin–bromate complex at 530 nm (40 mm cell).

reagent for 25 ml of sample was the adopted procedure, because of the better signal stability in comparison to the addition of 0.5 ml of reagent.

Blank measurements

In Table 1 replicate absorbance measurements of blank solutions in deionized water and in bromate-free drinking water are reported. The results show good agreement between the two series of data, thus supporting the use of deionized water 'blanks' for bromate analysis in drinking water. Drinking water blanks were obtained including passage through the cationic exchange resin.

Linearity and detection limit

The regression plot in the concentration range 0–20 μg l^{-1} using a 40 mm cell is reported in Fig. 4 with the 95% level confidence limits. The statistical parameters for the linear regression model are reported in Table 2. A good correlation was obtained as can be observed from the correlation coefficient (r) and residual values. Using the same statistical software package the linearity of the calibration graph was demonstrated.

From the data reported in Table 2 and from the standard deviation value of 11 replicate measurements of blank solution a detection limit of 1 μg l^{-1} of bromate was calculated following the propagation of error approach suggested by IUPAC.[11]

The calculated detection limit allows bromate estimation in real drinking water samples without the need for preconcentration and is in accordance with the requirements of the European standards for drinking water quality, which fixed a limit value of 10 μg l^{-1} of bromate.

Table 1 Blank measurements (absorbance units) in deionized and drinking water

	Deionized water	Drinking water
	0.075	0.075
	0.077	0.076
	0.075	0.076
	0.076	0.076
	0.078	0.072
	0.075	0.073
	0.075	0.073
	0.077	0.074
	0.076	0.076
	0.076	0.076
	0.074	0.076
Average	0.075	0.075
s	0.001 (n = 9)	0.001 (n = 7)

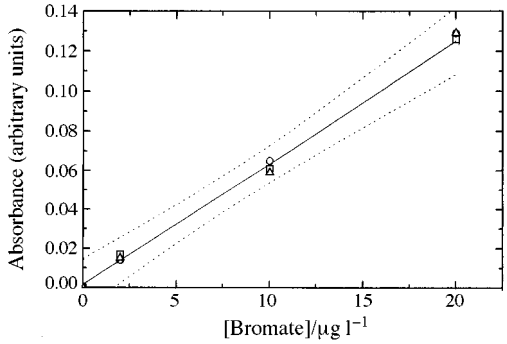

Fig. 4 Calibration graph for bromate in the range 0-20 μg l^{-1}. Solid line represents linear regression and dot lines are 95% confidence limits.

Table 2 Regression data and statistical parameters for bromate calibration in the range 0–20 μg l^{-1}

	Expected value	Standard error
Slope	0.0063	8.99×10^{-5}
Intercept	0.0007	0.001

Correlation coefficient (r) = 0.9990

Residuals—

x value/ μg l^{-1}	Mean Y (absorbance units)	Predicted Y (absorbance units)	Residuals (absorbance units)
0.000	0.0000	0.0007	−0.0007
2.000	0.0153	0.0133	0.0020
10.00	0.0617	0.0639	−0.0022
20.00	0.1280	0.1271	0.0009

Table 3 Comparison of absorbance readings for deionized and drinking water samples at 5 μg l^{-1} of bromate (blank value already subtracted)

	Deionized water	Drinking water
	0.047	0.042
	0.043	0.044
	0.044	0.045
	0.040	0.048
	0.043	0.048
Average	0.043	0.045
s	0.002 (n = 5)	0.002 (n = 6)

Interferences

The effects of some ions on bromate determination has been checked. Among the anions tested, sulfate, bromide, nitrate and chlorate did not interfere at normal concentration levels in drinking water.

Interference from cations was demonstrated for Ca^{2+}, Mg^{2+}, Zn^{2+} and Cu^{2+} at the concentrations found common in drinking water. These interferences were easily removed by passage through a strong cationic resin, as described in the procedure. The cationic nature of the interferences was also demonstrated by passing a drinking water sample through a column of anionic resin (IRA 400, chloride form): no interference attenuation was observed, thus excluding the presence of interfering anionic species in solution. This point was not investigated further in the present work.

Following the proposed procedure, a complete agreement between measurements in deionized water and in drinking water samples spiked with bromate solution at known concentration was found, as summarized in Table 3. Spiked drinking water samples and standard solution gave the same absorbance readings supporting the use of deionized water samples as calibration standards for bromate analysis in drinking water.

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