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Toxicity of Bromate Ions in Drinking Water and its Determination Using Ion Chromatography with Post Column Derivatisation

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Abstract

Disinfection of drinking water is usually carried out by chlorination. This is a well-known and effective technology which has many advantages. However, during this process dangerous by-products such as trihalomethanes, as well as chlorate and chlorite are formed.

The disinfection of bromide-containing source waters with ozone results in the production of bromate ions (BrO_3^-), which are formed as a result of a series of complex reactions between ozone and bromide ions present in water. Bromates are possible human carcinogens. For these reasons trace analysis of bromate and other oxyhalides by-products in waters has received considerable attention in recent years.

This article describes the determination of bromate in drinking water by IC with post column derivatisation using $NaBr/NaNO_2$ and UV detection. The direct method allows the determination of bromate at low $\mu g/dm^3$ levels and sample pretreatment is not necessary.

Keywords: bromate, drinking water, ion chromatography.

Introduction

A large part of distributed waters for human consumption must be effectively and frequently controlled. Waters used for the preparation of drinking waters are often contaminated with organic and inorganic substances and are biologically impure. It is therefore a necessity to purify and disinfect source waters in order to obtain waters of drinking quality.

Disinfection of source waters is in practice performed usually by chlorination procedure [1-3]. During the 1970s it was discovered that chlorination of drinking water produced carcinogens such as trihalomethanes, haloacetic acids and others [4-9]. Chlorite (ClO_2^-) and chlorate (ClO_3^-) are the disinfection by-products formed when chlorine dioxide (ClO_2) is used to disinfect drinking water [10,11]. Since then, environmental regulatory agencies, as well as drinking water treatment technologists, have been carrying out extensive research for alternative disinfection methods that minimize the production of by-products with significant health risks.

One of these alternative drinking water desinfection processes is ozonation, which has emerged as the most promising alternative to chlorination [12]. Due to the high oxidation-reduction potential of O_3 the possibility of direct oxidation by O_3 molecules and direct oxidation by radial-type reactions the application of this method in water treatment enables the removal of some inorganic substances (e.g. iron, manganese) and a complete or partial decomposition of natural organic substances (e.g. humic acids, aliphatic and aromatic hydrocarbons) [13].

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In spite of these undeniable advantages this method of water treatment can lead to some undefined hazards, especially concerning the formation of bromate in waters containing bromide.

Legube *et al*. [14] presents a survey of bromide and bromate values in raw waters and ozonylated waters in several European countries. Ozone dosage and total contact time with ozone, water temperature and pH value, initial concentration of bromide and the presence of organic carbon (e.g. TOC) have influence on the formation of bromate [15-17]. In 1993 the World Health Organisation (WHO) recommended setting a guideline of 25 μg/dm^3 for bromate ion in drinking water and estimated a lifetime cancer risk at 1 in 10^{-5} for bromate at 3 μg/dm^3 [18].

Recently the maximum contaminant level (MCL) of bromate in drinking water recommended by WHO and European Countries (EC) is 10 μg/dm^3 [19]. The same value came into force in Poland in 2000 [20].

This parameter has been primarily based on current analytical capability (not on toxicological considerations - the target concentration for bromate in drinking water is zero). Thus, there is a need for ongoing development and refinement of analytical technologies in order to permit rapid and reliable determinations at the submicrogram per litre level.

International Agency for Research on Cancer (IARC) classified bromate in group B-2 (as a "probable human carcinogen") and established a drinking water maximum contaminant level goal (MCLG) of zero and MCL of 10 μg/dm^3 for bromate in finished drinking water [21]. Depending on results of further research, a risk model could indicate a more definitive guideline value for oxyhalides in drinking water. The higher limit sets are mainly due to the lack of sensitive analytical methods for routine laboratories. For these reasons there is a need for improving existing methods in terms of sensitivity, cost and reliability.

Numerous techniques are used to determinate oxyhalide compounds including titration, colorimetric, spectrophotometric, flow injection analysis and capillary electrophoresis methods [22-24].

The majority of methods for the determination of bromate, chlorite and chlorate are usually carried out by ion chromatography (IC) combined with a variety of detection methods [25].

Much lower detection limits are obtained using hyphenated techniques such as ion chromatography coupled with mass spectrometry (IC-MS) [26-28]. These techniques are very sensitive and single analysis is cheap, but highly sophisticated, and the instrumentation is expensive. Anion analysis of water samples should be performed using a limited number of methods and they should be as inexpensive and simple as possible.

Another technique for the determination of inorganic desinfection by-products is IC coupled with a post-column reaction (PCR) followed by spectrometric detection [29,30]. The PCR method based on o-dianisidine was developed by Warner and Daniels [31]. The limit of detection of bromate in this method is 1 μg/dm^3. However, there are some disadvantages: poor resolution of bromate and chlorite ions and carcinogenic characteristic of o-dianisidine.

Determination of bromate by using fuchsin as a post-column reagent on μg/dm^3 level was described by Achilli and Romele [32]. In July 1997, the United States Environmental Protection Agency (US EPA) began sampling and analyzing water matrices from US municipalities serving populations greater than 100,000 for low-level bromate in support of the Information Collection Rule (ICR).

The US EPA has reported two methods capable of detecting bromate at or below promulgated MCL level 10 μg/dm^3. These methods are EPA Method 300.1 and 317.0 [33,34], which reduced the bromate detection limit from 20 μg/dm^3 to 1.4 μg/dm^3 using direct injection of the sample.

In a continuing effort to simplify the analysis and improve sensitivity for trace levels of bromate in drinking water in September 1998, US EPA presented postcolumn reagent method with o-dianisidine. Echigo *et al*. [35] described a comparison of three post-column methods for the analysis of bromate and nitrite in drinking water.

The regulatory standards for oxyhalides in drinking water require an analytical method with a detection limit of at least 25% of the parametric value. This method must be relatively simple, accurate, cheap and adequate for routine laboratories.

The International Standards Organisation (ISO) published in 1997 a method for determination of chlorate, chloride and chlorite in water with low contamination by using ion chromatography [36].

In 2000 an interlaboratory trial was organized involving 26 European laboratories using the draft standard IC method with conductivity detection and/or alternative methods. Three alternative laboratory-based methods were developed, based on ion chromatography coupled with different detection systems: ICP-MS, colorimetry or fluorimetry. The performance data of the three methods are at least comparable to the respective data of standard IC method [37].

The future application of the alternative methods will depend on the equipment of the laboratories and on the number and kind of samples to be analyzed. For the moment recommended method for determination of bromate in drinking water is IC/CD method established as ISO Standard 15061 in 2001 [38]. This standard consists of two parts - direct method and preconcentration method, but suffer from the existence of interferences which require a time-consuming step for elimination, clean-up and separation before the instrumental measurements.

This article describes the determination of bromate in water using IC and post column derivatisation with $NaBr/NaNO_2$ mix used as derivatisation reagent in order to form tribromide, which are detected using UV detector in specific wavelength 267 nm. The method allows the determination of bromate at low μg/dm^3 levels. The aim of this work was to evaluate the usefulness of a proposed method to determinate bromate in water samples as well

as calculation of limits of detection and quantification in waters with different matrixes according to ISO 8466-1 and DIN 32 645 standards.

Experimental Procedures

Ion chromatographic separations were performed on Dionex DX-500 ion chromatograph system (Sunnyvale, CA, USA) consisting of: gradient pump (GP 40), conductivity (ED 40) and UV detectors (AD 20), suppressor (ASRS II), rear-loading Rheodyne injection valve, autosampler ASM-2 (Dionex) and Peak Net Chromatography Workstation (Version 5.1).

Analytical grade sulfuric acid, sodium bromide, sodium nitrite, sodium bromate and sodium carbonate were obtained from Merck (Darmstad, Germany). Water used in the experiments was purified using Millipore equipment (Millipore, Bedford, MA, USA) and had a electrical conductivity < 0.05 μS/cm.

A 1000 mg/dm^3 bromate stock standard solution has to be prepared by dissolving sodium bromate in deonized water and then stored in a refrigerator at 2°C to 8°C. Calibration solution of bromate had to be prepared by diluting the stock standard solution to the required concentration just before use.

Separation conditions were as described below:

Columns	-	IonPac AG9-HC, AS9-HC;
Eluent	-	9.0 mM/dm^3 Na_2CO_3;
Flow rate	-	1.0 mL/min;
Injection volume	-	500 μL;
Detection	-	Conductivity;
Suppressor	-	ASRS II.

and post-column derivatization conditions:

Reagent	-	0.5 mol/dm^3 NaBr + + 20 mg/dm^3 $NaNO_2$
Reagent flow rate	-	0.5 mL/min;
Regenerent	-	0.75 mol/dm^3 H_2SO_4;
Regenerent flow rate	-	2 mL/min;
Reaction coil	-	500 μL;
Reactor temperature	-	60 ^{0}C;
UV detector	-	267 nm.

Results

A schematic flow diagram is shown in Fig. 1. The chromatography system consists of a large injection volume autosampler and a gradient pump to deliver the sodium carbonate eluent through guard (AG9-HC) and separator (AS9-HC) columns. The effluent flows through the suppressor device into the CD cell, where conductive inorganic anions are detected. Then effluent is directed to the T-junction to be mixed with the derivatisation reagent.

The derivatisation reagent HBr is generated by the reaction of NaBr/$NaNO_2$ solution with 0.75 mol/dm^3 sulfuric acid. This reaction takes place in a second sup-

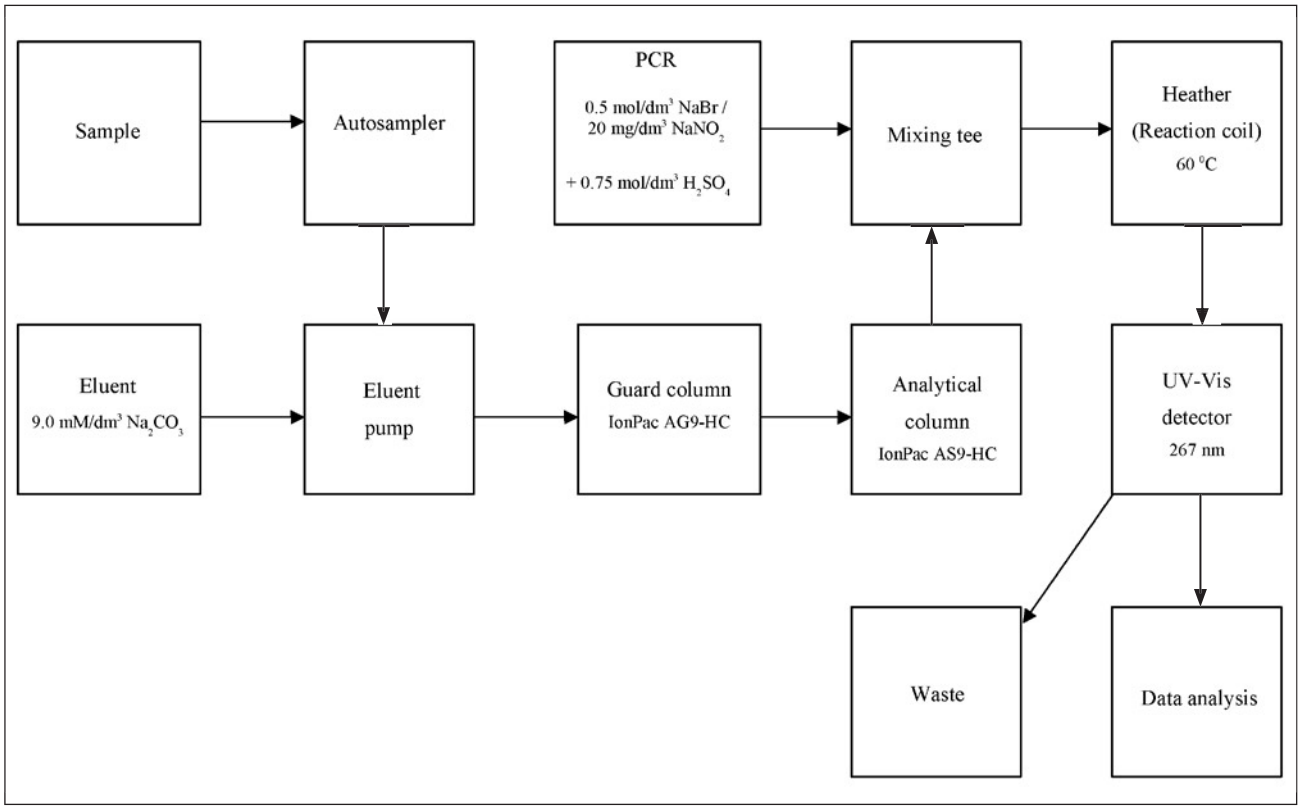

Fig.1. Schematic diagram of analytical system.

pressor device. Sulfuric acid is supplied to the suppressor with the help of helium head pressure. The $NaBr/NaNO_2$ solution is delivered by the reagent delivery pump. The formed HBr is mixed in the T-junction with the effluent from the CD.

Mix is then directed into the reaction coil placed in a column oven. The reaction coil volume and temperature have to be optimised to 60°C to produce maximum reaction yield. The tribromide ion is detected by UV at 267 nm [39].

This process depends on the fast, temperature-dependent reaction between the eluting oxyhalide and the bromide ion under acidic conditions according to equation (1):

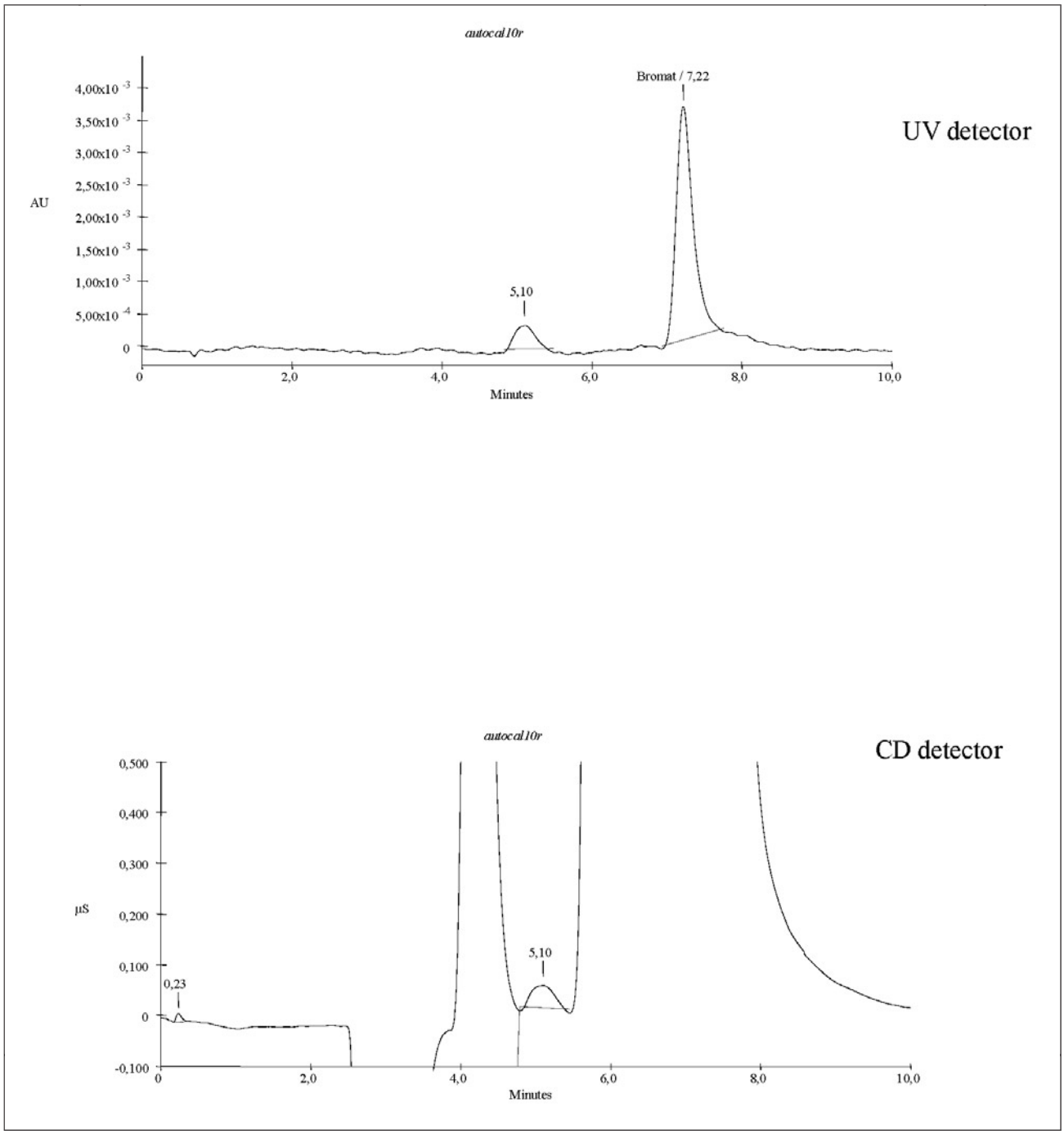

Fig. 2 Comparison of chromatograms obtained from UV and CD detectors.
Sample: tap water spiked with 1,0 µg/dm^3. Chromatographic conditions: Columns - IonPac AG9-HC, AS9-HC; Eluent - 9.0 mM/dm^3 Na_2CO_3; Flow rate - 1.0 mL/min; Injection volume - 500 µL; Detection - conductivity or UV; PCR reagent - 0.5 mol/dm^3 NaBr + +20 mg/dm^3 $NaNO_2$; Reactor temperature - 60ºC.

Table 1. Limit of detection and limit of quantification of bromate ions determined by IC with post-column reaction.

Parameter		Deonized water spiked with bromate		Tap water spiked with bromate	
Working range, [µg/dm^3]		0.2 – 2.0	0.5 – 5.0	0.2 – 2.0	0.5 – 5.0
Numbers of replicates		10	10	10	10
Standard deviation S_x, [µg/dm^3]	Peak area	0.10	0.26	0.04	0.09
	Peak height	0.10	0.25	0.03	0.09
Coefficient of variation, V_x [%]	Peak area	9.76	9.76	3.72	3.61
	Peak height	9.18	9.18	3.14	3.57
Limit of detection (LOD), [µg/dm^3]	Peak area	0.28	0.71	0.11	0.28
	Peak height	0.26	0.67	0.09	0.27
Limit of quantification (LOQ), [µg/dm^3]	Peak area	0.78	1.95	0.32	0.77
	Peak height	0.73	1.84	0.27	0.76

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O \quad (1)$$

In the presence of excess bromide, this reaction will proceed further to generate the tribromide ion according to equation (2):

$$Br_2 + Br^- \rightarrow Br_3^- \quad (2)$$

Iodate and chlorite also form UV active compounds with bromide. In described analytical conditions separation and determination of bromate ions on µg/dm^3 levels by using a conductivity detector is impossible because retention times of chloride and bromate anions are very similar. Chloride ions which are present in natural samples in several thousands times higher concentrations than bromate cause overlapping of their peaks.

To reduce the bromate detection limit and improve the sensitivity, derivatization followed by UV detection is necessary. Common anions such as chloride, nitrate and sulphate are invisible in UV detector in described analytical conditions. The appropriate composure of the post-column reagent mixture is responsible for the success of this method.

The generation of tribromide requires more bromide than protons; therefore, it is necessary to maintain a high background of bromide. The reaction (equation 1) needs to take place rapidly in order to maximise the yield of tribromide formation. Conversion of bromate to tribromide requires a reducing agent for an effective reduction in oxidation state from + 5 to -1/3. Due to the instability of HBr it must be generated at the time of reaction with bromate using a suppressor device.

The reagent mix of $NaBr/NaNO_2$ is passed through the interior side of the cation exchange membrane, while sulfuric acid passes over the exterior side of the membrane. Sodium bromide is converted into hydrobromic acid by cation exchange between sodium ion and proton.

Using the set-up described above it was possible monitoring the inorganic anions such as F^-, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} by suppressed CD and µg/dm^3 levels of bromate by UV detection. The high capacity column IonPac AS9-HC IonPac (55 % DVB with acryl/alkanol quaternary ammonium ions as functional groups, capacity 190 µeq) was especially developed to improve the separation between bromate and chloride.

Using IC-PCR method iodate and chlorite anions can also be detected using a UV detector. If those ions are the only anions of interest, then effluent from the analytical column can be directed to the T-junction bypassing the suppressor and CD.

Prepared 10 standard solutions of bromate in concentration ranges 0.2-2.0 µg/dm^3 and 0.5-5.0 µg/dm^3 in deonized and drinking water, respectively. Standard deviation (S_x) and coefficient of variation (V_x) were calculated according to ISO 8466-1. The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to DIN 32645. Data are shown in Table 1.

Results of a bromate repeatability study of IC-PCR method are described in Table 2. An example of obtained chromatograms for CD and UV detector is shown in Fig. 2.

This method was applied to determine common anions and bromate in raw water and ozonated drinking water from water treatment plants. The results are presented in Table 3.

Discussion

The described method is suitable for determining bromate in drinking water, because limit of quantification calculated from peak height or peak area is lower than 1 µg/dm^3. Limit of detection should be less than the 25% limit of acceptable concentration, in the case of bromate it means less than 2.5 µg/dm^3.

Parameters such as Var, TV and F-test can be used for the checking of equivalence between peak area and peak height evaluations. Because TV < F-test (except level 5.0

Table 2. Results from replicates IC-PCR method.

No	Level [µg/dm³]	Signal		X		S_x		V_x		Var		TV	F-test
		Area	Height	Area	Height	Area	Height	Area	Height	Area	Height		
1	0.5	10176	571	9877	561	208.44	8.90	2.11	1.59	4.45	2.51	1.77	< 5.19
2		9606	557										
3		9805	565										
4		9948	565										
5		9850	548										
1	1.0	16304	917	15991	932	396.5	43.83	2.48	4.70	6.15	22.09	3.59	< 5.19
2		15368	931										
3		15953	1008										
4		16366	898										
5		15967	909										
1	2.0	28388	1645	28026	1627	404.53	13.33	1.44	0.82	2.08	0.67	3.10	< 5.19
2		28472	1610										
3		27742	1628										
4		27533	1620										
5		27996	1634										
1	5.0	91869	5991	92488	5424	1841.8	395.8	1.99	7.3	3.97	53.2	13.4	> 5.19
2		90556	5206										
3		95542	5423										
4		92259	5392										
5		92216	5108										

Where:
No - number of replicate determinations;
S_x - standard deviation of the repeatability;
F-Test - value from the F-table (f=N-1; p 95%);
X - mean of Signal obtained from replicates;
TV - quotient of $(S_{x\ area})^2 / (S_{x\ height})^2$, TV must be > 1 for comparison for F-test.
Signal - measured peak area or height in [µV·s] or [µV];
Var - coefficient of variation;
Level - BrO_3^- concentration checked in [µg/dm³];
V_x - coefficient of variation of the repeatability in [%];

Table 3. Concentration [mg/dm³] of inorganic anions including bromate in the analyzed real water samples..

Sample	F^-	BrO_3^-	Cl^-	NO_3^-	Br^-	SO_4^{2-}
Raw water no.1	0.69	-	16.88	11.46	0.18	37.06
Ozonylated final treated water no.1	0.66	0.0065	16.83	11.54	0.17	37.28
Ozonylated final treated water no.1 spiked with 2.5 µg/dm³ of bromate	0.68	0.0092	16.78	11.14	0.17	37.30
Ozonylated final treated water no.2	0.98	0.0034	26.80	7.96	0.11	26.65
Ozonylated final treated water no.2 spiked with 2.5 µg/dm³ of bromate	1.00	0.0056	26.49	7.85	0.10	26.73

µg/dm³) both signals (peak area and height) may be used for calculations.

Data obtained for samples from Water Treatment Plant (Table 3) show that this method is applicable to determination of bromate in environmental samples.

Compared to the ISO 15061 standard this method is cheaper (sample pretreatment with special cartridges in unnecessary) and can be use as an alternative method. Very soon ISO will start study of one of the post column derivatization methods for the determination of bromate in drinking water [40].

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