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Original Papers

Bromate screening as an ozonation water disinfection by-product by sequential injection spectrophotometric method

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Abstract

The aim of this work was the development of an automatic sequential injection analysis method to monitor the ozonation process for water disinfection. The determination was based on the reaction between bromate and o-dianisidine in the presence of bromide in acidic medium. The determination parameters were studied and adjusted to enable bromate quantification in the range 0.35 – 4.0 mg BrO_3^-/L with a limit of detection of 20 µg BrO_3^-/L. The choice of a sequential injection procedure enabled a minimal consumption of reagents and no need for sample pre-treatment. The developed sequential injection proved to be accurate with < 5% relative deviation when compared to ICP-MS and an average of 101% in recovery percentages studies. It was effectively applied to monitor an ozonation process enabling the follow up of the process with real-time quantification of the bromate content.

Introduction

Sodium and potassium bromate are chemical compounds widely used in textile or food industries; however they do not occur naturally in water [1]. Bromate, specifically potassium bromate, is an antioxidant agent that only appears in water as a result of industry pollution, as a consequence of contaminated soil or when formed in some water treatment [1]. Furthermore, bromate has been related with adverse health effects [2] and has been categorized as potentially carcinogenic to humans by the International Agency for Research on Cancer [1], which is why its monitorization in waters has gain importance in the last few years.

Water safety is a major concern, so it is essential to monitor and treat it. Different methodologies have been used for water disinfection such as chlorination, membrane filtration, UV treatment, ozonation and others to effectively inactivate microorganisms present in the water [3]. Despite being highly effective in water disinfection, ozonation has also been associated with the production of toxic disinfection by-products namely as bromate [3,4]. Bromate formation is particularly problematic since it is not biodegradable in the commonly use biological filters employed after the ozonation process [5]. Consequently, several methods for bromate determination, mostly in water, have been reported (Table 1) such as ion chromatography [6], HPLC [7,8], chemiluminescence [9] and spectrophotometric methods [10–14]. In most those works the application range is quite similar ranging from about 1 μg/L (0.008 μM) to about 1 mg/L (8 μM), including a couple of flow-based approaches [10,12,13]. Therefore, without loss of sensitivity, the flow-based approaches represent a faster, effective alternative for the bromate determination as shown with quantification rate of up to 46 h^{-1} reported by Tóth et al. [10].

In this work, the development of a sequential injection (SI) methodology using o-dianisidine (ODA) for bromate spectrophotometric determination is described. The SI

technique is known for key features namely automation, versatility, and real-time analysis and has been extensively used as a water monitoring tool [15]. The versatility and feasibility of SI in incorporating in-line treatments is vital in adjusting to the colour reaction specific demands [16–18] and was decisive for its choice. The chosen reaction between bromate and and o-dianisidine (ODA) consists in the formation of Br_2 (with bromide in excess) and consequent bromination of ODA in acid medium. The orange-brown product can be spectrophotometrically detected at 450 nm, thus enabling the bromate quantification [19,20]. The developed SI technique was studied to attain the best reaction parameters and resulted in a high selective, automatic method for the real-time determination of bromate during an ozonation process (and natural waters) with no need of sample pre-treatment.

Experimental

Reagents and solutions

All solutions were prepared with analytical grade chemicals and Milli-Q water (resistivity > 18 MΩ cm, Millipore).

A potassium bromate (Merck) stock solution was daily prepared by dissolving 3 mg of the solid in 250 mL water. Working standard solutions within the range 0.35 - 4 mg/L were prepared from the previous solution.

The reagent solution was prepared by dissolving 25 mg of *o*-dianisidine, ODA (Sigma-Aldrich) and 230 mg of potassium bromide (Merck) In 50 mL of 1 M of HNO_3, resulting in 2 mM of ODA and 0.04 M of KBr (a 1:20 ODA: KBr proportion). The reagent solution was left to stabilize overnight before use and then was stable for at least fifteen days.

The 1 M of nitric acid solution was prepared by dilution of the commercial solution (d = 1.39; 65%, Merck).

Sequential injection manifold and procedure

The developed sequential injection (SI) method for bromate determination is depicted in Fig. 1.

The SI manifold consists of a peristaltic pump (Minipuls 3 Gilson®) connected to the central of channel of a 10-port selection valve (Valco Cheminert ™), where the reagent and standard/samples solutions are placed. A reaction coil with 80 cm length was placed in a thermostatic bath (ISCO GTR 190) at 35 ºC on the way to the detection, in a lateral port of the selection valve. An Ocean Optics HR 4000 High-Resolution charged coupled device detector (CCD), equipped with a pair of 400 μm optical fibers (Ocean Optics P400-2-UV/VIS) and a Micropack DH-2000 deuterium halogen light source, was used as the detection system. A Hellma 178.011-OS flow-cell with 10 mm light path and 30 μL inner volume was used. Data acquisition signal was obtained at 450 nm and it was performed through the OceanOptics – Spectrasuite software running in a personal computer (HP L1706). All the tubing connecting the different components consisted of 0.8 mm PTFE tube (Omnifit). The protocol sequence for the bromate determination is detailed in Table 2.

The determination of bromate was initiated by the sequential aspiration of color reagent and standard/sample plugs into the holding coil (Steps A and B). Then, the flow was reversed, promoting the mixture of the two plugs and directing them to the reaction coil immersed in the thermostatic bath at 35 ºC for a stop period of 30 s (Steps C and D). Finally, the formed colored product was propelled to the detector for absorbance measurement at 450 nm (Step E).

Sample collection and ozonation process

Well water samples (up to about 10 L) were collected (Northwestern, Portugal) and stored in the refrigerator at 4ºC before use.

For the ozonation process, the well water sample was subdivided into three different sub-samples of 2 L each: one was set as reference (WW1); one was spiked with 3 mg/L of potassium bromide (WW2); and one spiked with of 6 mg/L of potassium bromide (WW3). The three sub-samples were then bubbled with ozone for 1 hour using an ozone generator (Hager®) and 100 mL aliquots were taken every 15 minutes for bromate quantification.

Reference procedure

The accuracy of the developed SI method was assessed by comparing the results obtained with the results acquired with an iCAP™ Q Inductively coupled plasma - mass spectrometry (ICP-MS) from Thermo Fisher Scientific (Bremen, Germany).

Results and Discussion

In order to optimize the SI system and improve the sensitivity of the method, several parameters were studied, namely the colour reagent composition, the reagent and sample volumes, among others. The studies were carried out by establishing calibration curves, and choose the conditions corresponding to the highest slope.

Preliminary studies – reaction kinetics

The reaction kinetics was evaluated in a batchwise approach performed at room temperature using bromate standards within the range 0.5 – 3.0 mg/L and using 1 mL of reagent to 2 mL of standard/sample.

The absorbance increase for each standard was registered for 10 min (ESI Fig.1) and it was clear that there was a significant increase up to 5 min (300 s), in particular for the highest concentrations, then stabilizing just before 10 min. So, calibration curves were established with the registered values at 60, 120, 180, 240 and 300 s (ESI Fig.2). The sensitivity, calibration curve slope, increased with increasing reaction time, but the increase became less significant, < 10%, from 240 s to 300 s (about 7% increase).

Reaction kinetics – sequential injection protocol

The first study in flow approach was to implement a stoppage time in the sequential injection protocol.

The same volume proportion of 1 reagent: 2 standard was used: 180 µL reagent and 360 µL of standard. Stop periods, set to be at the detector, were tested ranging from 0 (no stop period) to 30 s (ESI Fig.3).

The sensitivity increased with the increase of the stoppage time; with a 10 s stop period the sensitivity was over 50% higher than without stop period. That increase was smaller for higher stoppage periods (i.e. from 10 to 15 s increased only about 20% and from 25 to 30 s below 10%). Nevertheless, the stoppage period of 30 s was set and used in the following studies.

In parallel, the impact of the flow rate was also evaluated for the propelling steps, as these are the ones relating to the reaction mixture and kinetics. The aspiration of reagents was set to a 60 µL/s flow rate to minimize dispersion and enable a faster cycle. However for the propelling steps, before the stop period, having a lower flow rate, 40 µL/s, resulted in a better mixture (increase about 5% the slope) and lower refraction index, respectively.

Sample/Standard volume study

With the stop period set to 30 s, the influence of the sample volume on the calibration curve parameters was tested and volumes of 300, 360, 420, 480 and 540 µL were studied (Fig. 2 A). The sensitivity increased up to 360 µL (highest slope was obtained) and then kept quite stable so 360 µL was the chosen volume.

Study of color reagent volume and composition

Then, having established the sample/standard volume, the color reagent volume and composition were studied. The volume of 300 µL was chosen from the tested volumes of 120, 180, 240, 300 and 360 µL (Fig.2 B). The sensitivity increased with the increase of the reagent volume but, although there was a significant increase up to 300 µL (> 20%), it became negligible from 300 to 360 µL (< 10%). Therefore, in order to avoid the unnecessary reagent consumption, the volume chosen was 300 µL.

Three reagent proportions of o-dianisidine (ODA) and potassium bromide (ODA : KBr) were studied: 1:50, 1:20 (proportion initially used), 1:10 and 1:5 (Fig. 3 A). For the 1:5 proportion, there was no correlation between the absorbance signal and the bromate standards. The highest sensitivity was obtained with the 1:20 proportion so it was the chosen proportion.

Reaction temperature

The ODA bromate reaction is temperature dependent [19,20]. Therefore, three temperatures were studied, namely 25 ºC (room temperature, RT), 35 ºC, 45 ºC and 55ºC (Fig. 3B). At 55 ºC, the in-line bubble formation interfered with the signal reading, making it impossible to distinguish from air bubbles caused signals, and so this temperature was discarded.

As expected, the sensitivity (calibration curve slope) increase with the temperature increase. As the increase was higher from the RT to 35 ºC (11%) then from 35 ºC to 45 ºC (< 6%) and considering the problem of bubbles formation, the chosen temperature was 35ºC.

Interferences studies

The potential interference of some anions (SiO_3^-. NO_2^-. NO_3^- and Cl^-) was assessed by calculating the interference percentage (IP). To calculate the IP, mixed standards with bromate (2.0 mg/L) and different concentrations of the potential interference ion were prepared (Table 3). The absorbance signal of the mixed standard (A_{Anion}) and the absorbance signal of the bromate standard ($A_{BrO_3^-}$) were used in the Eq. (1).

$$IP\ (\%) = \left[\frac{\left(A_{Anion} - A_{BrO_3^-}\right)}{A_{BrO_3^-}}\right] \times 100 \qquad (1)$$

The tested concentrations for each tested anion correspond to suggested values and maximum admissible concentration in natural waters [1]. It was considered that to be no interference when the calculated IP < 10%. Therefore, there were no significant interferences from the tested anions.

Analytical features of the developed method

Having finished the studies for optimization of the developed SI method for bromate determination, the main features are summarized in Table 4.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated according to IUPAC recommendation [21,22] as the concentration corresponding to three and ten times, respectively, the standard deviation of ten consecutive blank signals. The

concentrations were calculated by interpolating, in the calibration curve, the blank signal average plus three (LOD) or ten (LOQ) times the standard deviation of ten blank signals. This mathematical calculation resulted in a significant difference between the LOD and LOQ and some samples were analysed between those values.

The determination rate was calculated based on the time per cycle, which according to the described protocol (shown in Table 2) plus the equipment's response, takes 95 seconds. The consumptions values were calculated per determination, corresponding to one full cycle. The inter day and intraday repeatability of the developed SI was assessed by calculating relative standard deviation (RSD) of calibration curve slopes.

For the intraday repeatability, a RSD = 1% was obtained from four calibration curves; for the inter day repeatability, a RSD = 9% was obtained from five calibration curves established over a 15-days period.

Method validation – Accuracy assessment

To evaluate the accuracy of the developed SI method three well water samples were analysed (WS1, WS2, WS3) and the values obtained compared to the reference procedure ICP-MS. All samples were analysed in triplicate. WS1 was spiked with bromide (about 1.5 mg/L) and ozonized for 30 min; WS2 was not ozonized and no bromide addition was made; to WS3, no bromide was added but it was ozonized for 30 min. As expected, the bromate concentration values for WS2 and WS3 were quite low, below the calculated LOQ; however, as the values were above LOD, and quite similar to those of the ICP-MS analysis, the results are presented anyway.

The calculated RD between the two sets of results were: RD_{WS1} = 3% (1.48 ± 0.02 mg/L BrO_4^- by ICP-MS and 1.53 ± 0.01 mg/L with the developed SI method); RD_{WS2} = 1% (0.051 ± 0.001 mg/L BrO_4^- by ICP-MS and 0.052 ± 0.014 mg/L with the developed SI

method); RD_{WS3} = - 6% (0.033 ± 0.001 mg/L BrO_4^- by ICP-MS and 0.031 ± 0.005 mg/L with the developed SI method).

The WS1 sample was also analysed prior to the ozonation process and, as expected, the values did not match as the ICP-MS accounts for total bromine, and the developed SI method accounts for bromate.

To further establish accuracy, recovery percentages were calculated according to IUPAC recommendations [23] using both natural and ozonised water (Table 5).

Well waters samples were spiked with bromate using 100 and/or 300 µL of a 160 mg BrO_3^- /L stock solution to a final volume of 20 and/or 50 mL of well water (W). Then, samples were analysed with the developed SI method and the recovery percentage calculated (Table 5) according to the Eq. (2).

$$\%R = \left([BrO_3^-]_{found} - [BrO_3^-]_{initial}\right) \div [BrO_3^-]_{added} \quad (2)$$

To validate the full range of the calibration curve, some of the well water samples used were previously ozonized (OW) which explains the high initial values observed. The average percentage for recovery tests was 101% with a standard deviation of 11% and the calculated T value was 0.417 for a critical T value 2.423, indicating that there was no evidence of matrix multiplicative interferences.

Method application – Application to the ozonation process

The developed SI method was applied to the entire ozonation process of three well waters (WW1, WW2, WW3), as described in section 2.3., by analysing the aliquots collected every 15 min up to one hour (Fig. 4).

The well waters had different initial content of bromide, resulting in significant differences in the formed bromate. Even with short ozonation time (15 min) the bromate

formation corresponds to ¼ of the initial bromide content. Therefore, a natural water with more than 40 µg/L of bromide cannot undergo ozonation process for more than 15 min in order to comply with the legal limit of 10 µg/L of bromate.

In both WW#2 and WW#3 (with high content of bromide), when the concentration of formed bromate was above 2.0 mg/L, apparently a parallel reaction between bromide and bromate occurred and caused bromate concentration to decrease, probably due to the production of bromine (Br_2). This parallel reaction causes the bromate concentration to decrease and when it becomes below 2.0 mg/L apparently the parallel reaction stops causing the bromate concentration to increase again.

Conclusions

The proposed SI method for bromate determination is highly effective to monitor water ozonation process. Being the maximum acceptable concentration of bromate in drinking waters of 10 µg/L, identical to the developed SI LOD, it is a useful tool to ensure that the regulations enforcement. Although there is no significant improvement in the attained LOD when compared to other flow procedures in Table 1 the quantification range is wider enabling to perform an effective monitoring of ozonation processes. The developed methodology proved to be fast and reliable with a high determination rate (37 determination/h) and a good repeatability (interday RSD = 9%). These features could be essential in a potential in-line application to the water ozonation process.

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Table 1 Summary of the some reported methods for bromate determination in water samples; LOD, limit of detection; FS, flow system; FI, flow injection; MSFIA, multi syringe flow injection analysis.

Target sample	**Method of detection/ determination**	**Dynamic range**	**LOD**	**Quantification rate**	**Reference**
Water (disinfection process)	Spectrophotometric / SI	0.30-4.0 mg/L	10 µg/L	37 h^{-1}	This Work
Drinking water	Chromatography	2 – 50 µg/L	0.1 µg/L	n.r.	[6]
Water	Chemiluminescent / FS	0.36 – 500 µM (0.046 – 64 mg/L)	0.08 µM (10 µg/L)	n.r.	[9]
Bottled water	Spectrophotometric / FI	1 – 20 µg/L	0.2 µg/L	46 h^{-1}	[10]
Water	Spectrophotometry	1 – 799 µg/L	0.67 µg/L	n.r.	[11]
Ozonized water	Fluorimetric / FI	4 – 200 µg/L	0.9 µg/L	10 h^{-1}	[12]
Water	Spectrophotometric / MSFIA	25 – 750 µg/L	6 µg/L	35 h^{-1}	[13]
Drinking water	Spectrophotometry	0 - 20 µg/L	1 µg/L	n.r.	[14]

n.r. - not reported

Table 2 Sequence protocol of the developed SI method for bromate determination in waters

Step	Port	Time (s)	Flow Rate (µL/s)	Volume (µL)	Description
A	1	5	60	300	Aspiration of the colour reagent
B	2-8	6	60	360	Aspiration of sample/standard
C	9	15	40	600	Propelling the mixture to the thermostatic bath reaction coil
D	9	30	0	-	Stop period
E	9	38	40	1520	Propelling to detector for absorbance measurement and signal registration

Table 3 Assessment of potential interferences of other anions studied by calculation of the interference percentage in the absorbance signal.

Potential interfering anion	**Tested concentration**	**Interference percentage (IP)**
SiO_3^-	15 mg/L	5%
NO_2^-	1.0 mg/L	2%
NO_3^-	50 mg/L	3%
Cl^-	1.0 g/L	3%

Table 4 Features of the developed method for bromate determination

Dynamic range (mg/L)	0.35 – 4.0
Calibration curve [1]; A = S x [BrO_3^-] mg/L + b	A = (0.102 ± 0.003) [BrO_3^-] + (0.124 ± 0.015); R^2 = 0.9992 ± 0.0002
LOD (μg/L)	20
LOQ (μg/L)	312
Determination rate (h^{-1})	37
Effluent volume (mL)	2.7
Consumption per determination	ODA 150 μg; KBr 1.7 mg; HNO_3 19 mg

[1] *n = 4*

Table 5 Recovery percentages for accuracy validation using well water (W) and ozonized well (OW) water with prior addition of bromate; SD, standard deviation; LOD, limit of detection.

Water source	Sample ID	Initial		Added	Founded		Recovery, %
		mg BrO_3^- /L	SD	mg BrO_3^- /L	mg BrO_3^-	SD	
well water	W#1	< LOD		0.774	0.763	0.032	99%
				2.321	2.554	0.05	110%
	W#2	< LOD		0.325	0.335	0.056	103%
	W#3	< LOD		0.325	0.298	0.092	92%
	W#4	< LOD		0.325	0.306	0.016	94%
	W#5	< LOD		0.325	0.328	0.077	101%
	W#6	< LOD		0.325	0.278	0.023	86%
ozonized well water	*OW#1*	*0.231*	*0.001*	0.797	1.127	0.057	112%
				2.390	2.912	0.028	112%
	OW#2	0.482	0.007	0.797	1.368	0.027	111%
				2.390	2.623	0.062	90%
	OW#3	*0.178*	*0.031*	0.797	0.935	0.022	95%
				2.390	2.466	0.073	96%
	OW#4	2.45	0.05	0.797	3.334	0.036	111%
				2.390	5.115	0.029	111%
	OW#5	3.83	0.01	0.797	4.728	0.022	113%
				2.390	6.275	0.037	102%
	OW#6	4.94	0.07	0.797	5.630	0.027	87%
				2.390	7.211	0.066	95%
	OW#7	3.03	0.02	0.797	3.778	0.038	94%
	OW#8	1.26	0.03	2.390	3.819	0.029	107%

Note: the values in italic are below LOQ but above LOD

Figure Captions

Fig. 1 Manifold of the developed SI methodology for the bromate determination in natural waters: P, peristaltic pump; HC, holding coil with 3 m; SV, selection valve (# 10 ports); S1-S6, Standard/sample solutions; W, waste; R_1, reaction coil with 80 cm; T, thermostatic bath at 35 ºC ; λ, spectrophotometer detector at 450 nm.

Fig. 2 Study of the sample (A) and reagent (B) volumes upon the calibration curve slope (○) and intercept (□); the points in full correspond to the slope and intercept values of the chosen volumes; the error bars represent 5% error.

Fig. 3 Study of the effect of reagent composition (A) and reaction temperature (B) upon the calibration curve slope; the darker bars represent the chosen conditions; the error bars represent 5% error.

Fig. 4 Monitoring the ozonation process of three well water (WW) samples: with no addition of bromide (WW #1), with addition of 3 mg KBr/L (WW #2), and with addition of 6 mg KBr/L; the error bars represent the standard deviation.

Figure 1

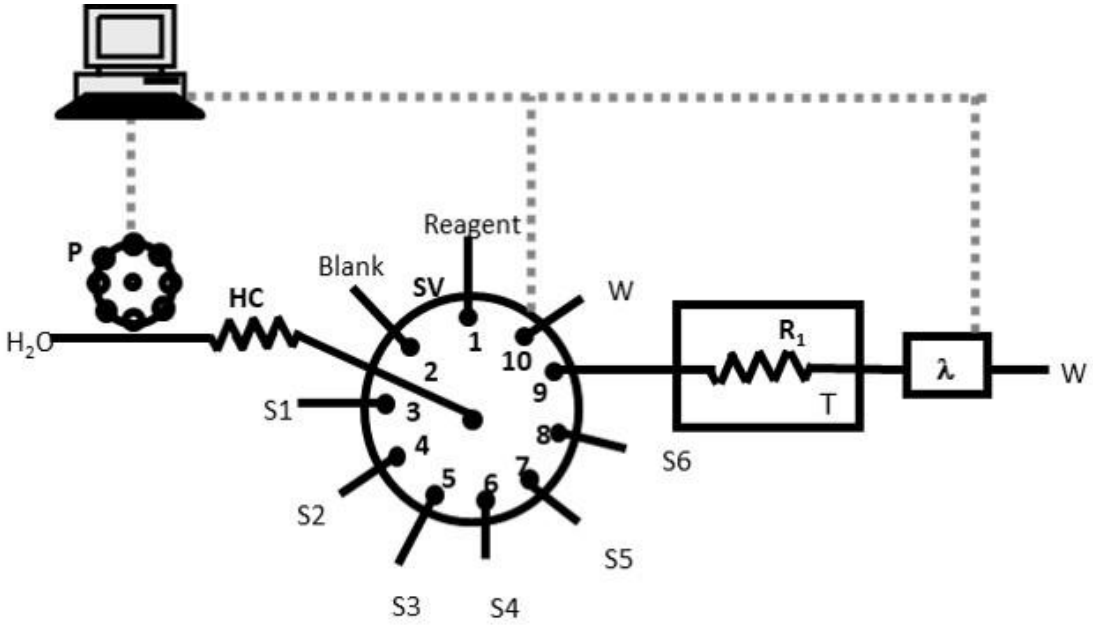
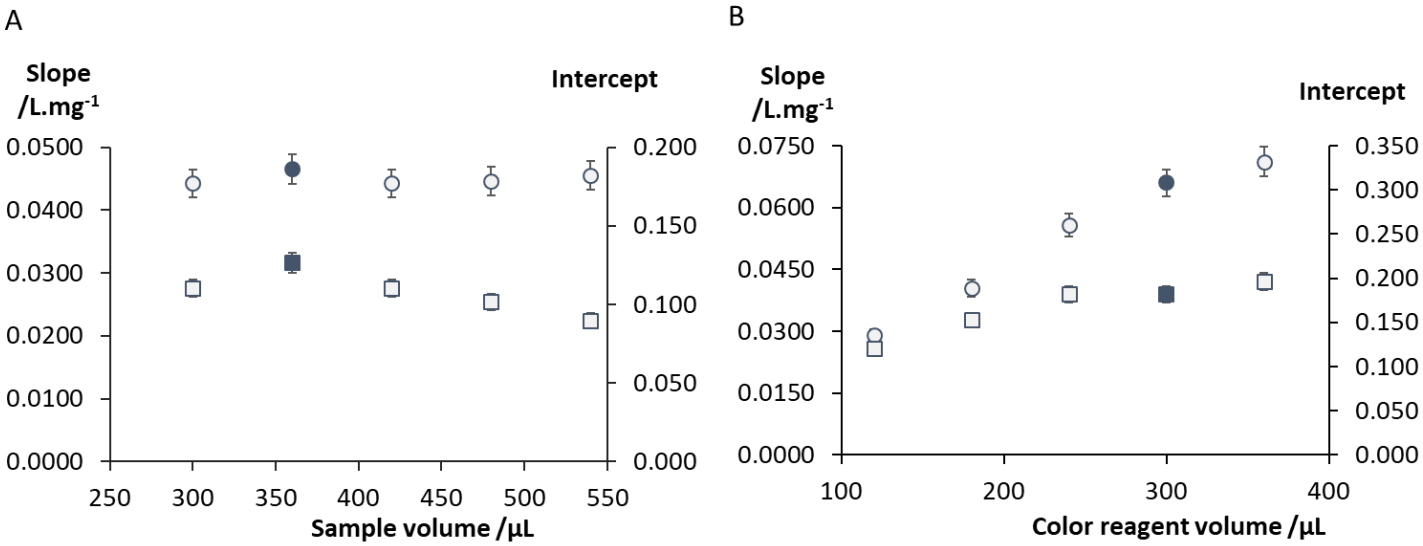


Figure 2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Slope /L.mg-1
Intercept
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0.0000
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0.150
0.100
0.050
0.000
250
300
350
400
450
500
550
Sample volume /µL
B
Slope /L.mg-1
Intercept
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0.0600
0.0450
0.0300
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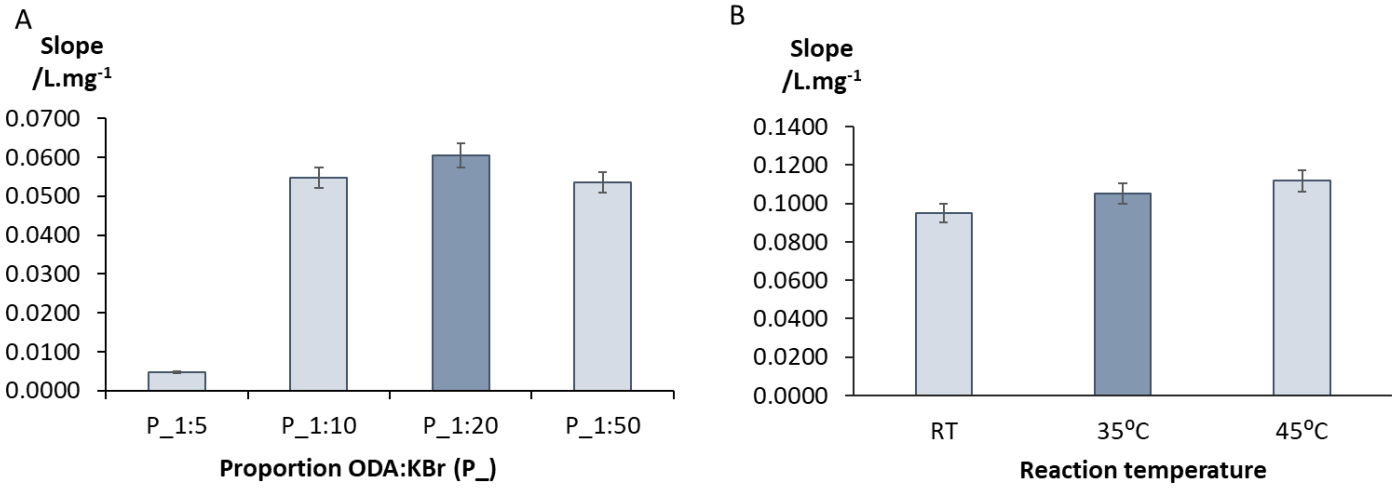
0.050
0.000
100
200
300
400
Color reagent volume /µL

Figure 3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0.0400
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P_1:5
P_1:10
P_1:20
P_1:50
Proportion ODA:KBr (P_)
B
Slope
/L.mg-1
0.1400
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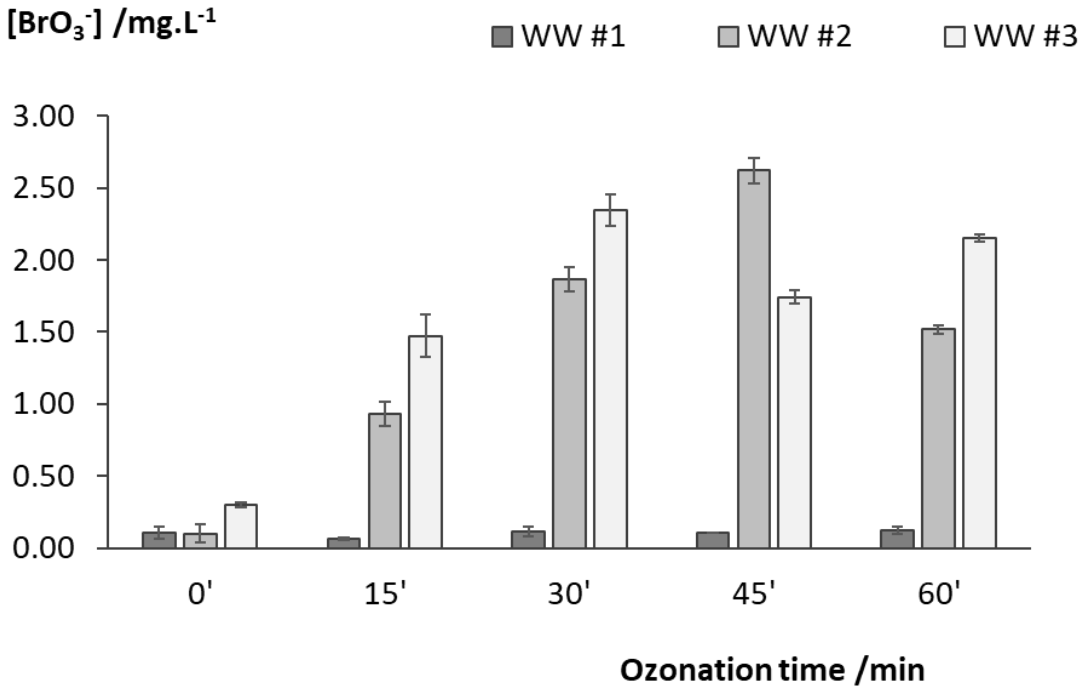
0.0400
0.0200
0.0000
RT
35°C
45°C
Reaction temperature

Figure 4


[BrO3-] /mg.L-1
WW #1
WW #2
WW #3
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0'
15'
30'
45'
60'
Ozonation time /min