Analysis of oxyhalides in water by ion chromatography–ionspray mass spectrometry

L. Charles[a,*], D. Pépin[b]

[a]*Institut Louise Blanquet, Facultés de Médecine et de Pharmacie, 63000 Clermont-Ferrand, France*
[b]*Chaire d'Hydrologie et Hygiène, Facultés de Médecine et de Pharmacie, 63000 Clermont-Ferrand, France*

Abstract

A sensitive method for analyzing chlorite, chlorate, bromate and iodate in water by ion chromatography (IC) coupled with ionspray tandem mass spectrometry (IS-MS–MS) has been developed. Prior to analysis, samples were subjected to off-line sample clean-up with Ba, Ag and H-form resins to remove sulfate, chloride and hydrogencarbonate, respectively. Oxyhalides in the purified samples were concentrated and separated on a short, high-performance anion-exchange column. An eluent consisting of ammonium nitrate in methanol–water (9:1, v/v) was found to be suitable for separating the analytes, while providing enhanced detector sensitivity. The coupling of IC with IS-MS–MS allows for the identification of the four oxyhalides mentioned above in a single run with very high specificity and sensitivity. © 1998 Elsevier Science B.V.

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1. Introduction

The occurrence of oxyhalide ion in drinking water is mainly due to disinfection processes. The oxidation of inorganic and organic compounds by chlorine dioxide is accompanied by the formation of chlorite, chloride and chlorate [1]. Since these oxychlorine species are potentially toxic, current regulations governing concentrations of chlorite and chlorate in drinking water supplies are becoming increasingly strict. The World Health Organization has proposed a provisional guideline value of 200 µg/l for the concentration of chlorite in drinking water [2]. During the last ten years, the use of ozone is spreading in the treatment of drinking water, to improve taste, odor, organic and inorganic micropollutant removal and to control chlorination by-product formation. Ozone, however, forms several organic

and inorganic by-products that are of growing concern, e.g. bromate, a known animal carcinogen [3]. Bromate is formed as a result of a series of complex reactions between ozone and bromide ions present in water. The maximum allowable level of bromate presently proposed by the US Environmental Protection Agency (EPA) is 10 µg/l, because of serious problems in bromate analysis at sub-ppb levels, as required by the toxicological threshold (0.05 µg/l). During ozonation, iodide ions may form iodate, but no data are available for iodate ions. Numerous techniques are used to analyze oxyhalide compounds, including colorimetry [4], amperometry [5], polarography [6], capillary electrophoresis [7], pulsed electrochemical detection [8] and suppressed conductivity [9,10]. Some are subject to interference, some are not sensitive enough and none of them are specific. A significant amount of interest has been focused on utilizing electrospray mass spectrometry (ESI-MS) in the analysis of inorganic species. Since

the analyte exiting the column is ionic in solution, it is possible to ''evaporate'' ions directly from the condensed phase into the gas phase. This may be readily accomplished by the ionspray (IS) LC–MS interface. The ionspray inlet produces charged droplets. As the solvent evaporates, the electric field increases and the ions move to the surface. At some critical field strength, ions are emitted from the droplets. Factors that seem to favor this process include the presence of organic solvents, low ionic strength of buffers, the absence of inorganic non-volatile salts and the presence of the analyte as cation or anion in solution. Classical ion chromatography (IC) eluents (such as borate or carbonate–hydrogencarbonate solutions) are incompatible with an IS-MS–MS system. These high-ionic-strength eluents suppress analyte ion signals and/or raise background ion counts, increasing limits of detection (LODs). The requirement for chemical noise reduction in the mass spectrometer is analogous to the importance of background conductivity suppression in IC. Reducing the electrolyte concentration in the chromatographic eluent by passing it through an ion-exchange fiber or continuously removing sodium ions by use of a membrane ion suppressor [11] allows good sensitivity. The proposed alternative is to select an electrolyte that is a good ionic eluent for oxyhalides and is also IS compatible. Our previous work on bromate analysis [12] showed that the use of such an electrolyte allows the advantages of IC selectivity to be combined with MS specificity and sensitivity.

2. Experimental

2.1. Reagents

Deionized water was obtained from a Milli-Q reagent water system (Millipore, El Paso, TX, USA). HPLC-grade methanol, sodium carbonate (Na_2CO_3, 99.9%) and sodium hydrogencarbonate ($NaHCO_3$, 99.5%) were purchased from Merck (Darmstadt, Germany). Ammonium nitrate (NH_4NO_3, ACS grade), potassium bromate ($KBrO_3$, 99.8%), potassium chlorate ($KClO_3$, 99%) and sodium chlorite ($NaClO_2$, ACS grade) were purchased from Alfa

(Karlsruhe, Germany). Potassium iodate (KIO_3, 99.8%) was from Fluka (Buchs, Switzerland).

2.2. Sample pretreatment

Removal of sulfate, chloride and bicarbonate anions from samples was performed using On-Guard-Ba, On-Guard-Ag and On-Guard-H cartridges, respectively, obtained from Dionex (Sunnyvale, CA, USA). The resin cartridges were individually rinsed with 5 ml of deionized water at a maximum flow-rate of 2 ml/min. The three cartridges were then connected together in the order Ba–Ag–H and installed on a vacuum manifold (Supelco, Bellefonte, PA, USA). A 10-ml sample was loaded at a maximum flow-rate of 2 ml/min. The first 3 ml was discarded, and a minimum of 6 ml was collected in a tube. A sparge with helium gas at 5 p.s.i. for 5 min was performed to remove dissolved carbon dioxide (1 p.s.i.=6894.76 Pa).
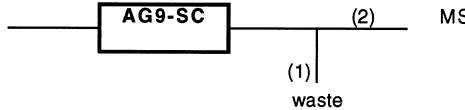
2.3. Chromatography

IC was performed with an LC 200 binary pump (Perkin-Elmer, Norwalk, MA, USA) and direct introduction of the samples was done with an infusion pump (Model 22) from Harvard Apparatus (South Natick, MA, USA). Flow injection analysis (FIA) was carried out using a Rheodyne 81-25 valve (Cotati, CA, USA). An injection volume of 20 μl was used.

IC of oxyhalide was carried out with an IonPac AG9-SC guard column from Dionex. The chromatographic steps are listed in Table 1. The column was connected to the detector only during the elution step. To obtain the appropriate flow-rate (50 μl/min) for ionspray ionization, the column effluent was split (ratio of 1:20) using a zero-dead-volume tee connector (Cluzeau Info-Labo, Sainte-Foy-La-Grande, France).

2.4. Mass spectrometer

Introduction systems were coupled to a Sciex API III Plus triple quadrupole mass spectrometer (Thornill, Canada) equipped with an atmospheric pressure ionization (API) source, via an IS interface. The starting resolution for both quadrupoles was set at

Table 1
Ion chromatography steps

Step	Duration (min)	Composition of pumped solution	Flow-rate (ml/min)	Purpose	Valve position
1	5	Water–methanol (10:90, v/v)	2	Conditioning	1
2	3	Sample	2	Sample loading	1
3	5	Water–methanol (10:90, v/v)	2	Conditioning	1
4	15	Water–methanol (10:90, v/v), 65 mg/l NH_4NO_3	1	Elution	2
5	3	200 mM Na_2CO_3, 75 mM $NaHCO_3$	2	Regeneration	1
6	5	2.0 mM Na_2CO_3, 0.75 mM $NaHCO_3$	2	Regeneration	1

0.7 amu fwhh. The mass spectrometer was operated in the negative ionization mode. Tandem mass spectrometry (MS–MS) measurements were based on collision-induced dissociations, with a collision-activated dissociation (CAD) energy of 20 eV. Ultra high pure (UHP) argon was the target gas, at a collision gas target (CGT) value of $300 \cdot 10^{15}$ molecules/cm^2.

Mass spectra of each oxyhalide were first achieved in product scan mode over m/z 20–200. The ions selected to be fragmented to yield oxyhalide spectra were m/z 67 and 69 for ClO_2^-, m/z 83 and 85 for ClO_3^-, m/z 127 and 129 for BrO_3^-, and m/z 175 for IO_3^-.

The chromatographic signal was recorded in multiple reaction monitoring (MRM) mode. Acquisition parameters are listed in Table 2.

Table 2
Mass spectrometer data acquisition parameters (multiple reaction monitoring)

Oxyhalide ion	Ion mass (m/z)	
	Q1	Q3
ClO_2^-	67.0	51.0
	69.0	53.0
ClO_3^-	83.0	67.0
	85.0	69.0
BrO_3^-	127.0	111.0
	129.0	113.0
IO_3^-	175.0	143.0
	175.0	159.0

Dwell time, 300 ms; pause time, 0.052 ms and duration, 15 min.

3. Results and discussion

3.1. ESI-MS–MS

Oxyhalides are ionic species of particular interest in mass spectrometry because of the natural occurrence of chlorine and bromine isotopic forms, ^{35}Cl and ^{37}Cl, and ^{79}Br and ^{81}Br. Thus, two precursor ions can be selected for ClO_2^-, for ClO_3^- and for BrO_3^-. Each precursor ion was selected in the first quadrupole (Q1) to be fragmented in the collision cell (second quadrupole, Q2), and product ions were analyzed in the third quadrupole (Q3). These spectra showed that oxyhalide fragmentation mainly consists of oxygen losses (Fig. 1). Signal will then be recorded in MRM, consisting of monitoring spectral transitions. Spectral transition monitoring from both isotopic forms for each analyte (Table 2) added to the chromatographic retention time information confers to the analysis a very high selectivity. No spectral interference can occur, the acquisition mode being extremely specific for each ion.

3.2. Eluent composition

In IS ionization mode, the use of organic solvent helps in the nebulization process and yields better ionic vaporization. FIA of individual oxyhalide standards in deionized water showed that mobile phase enrichment with methanol increased the detected signal: A mobile phase comprising 90% methanol provides optimal spray conditions, as
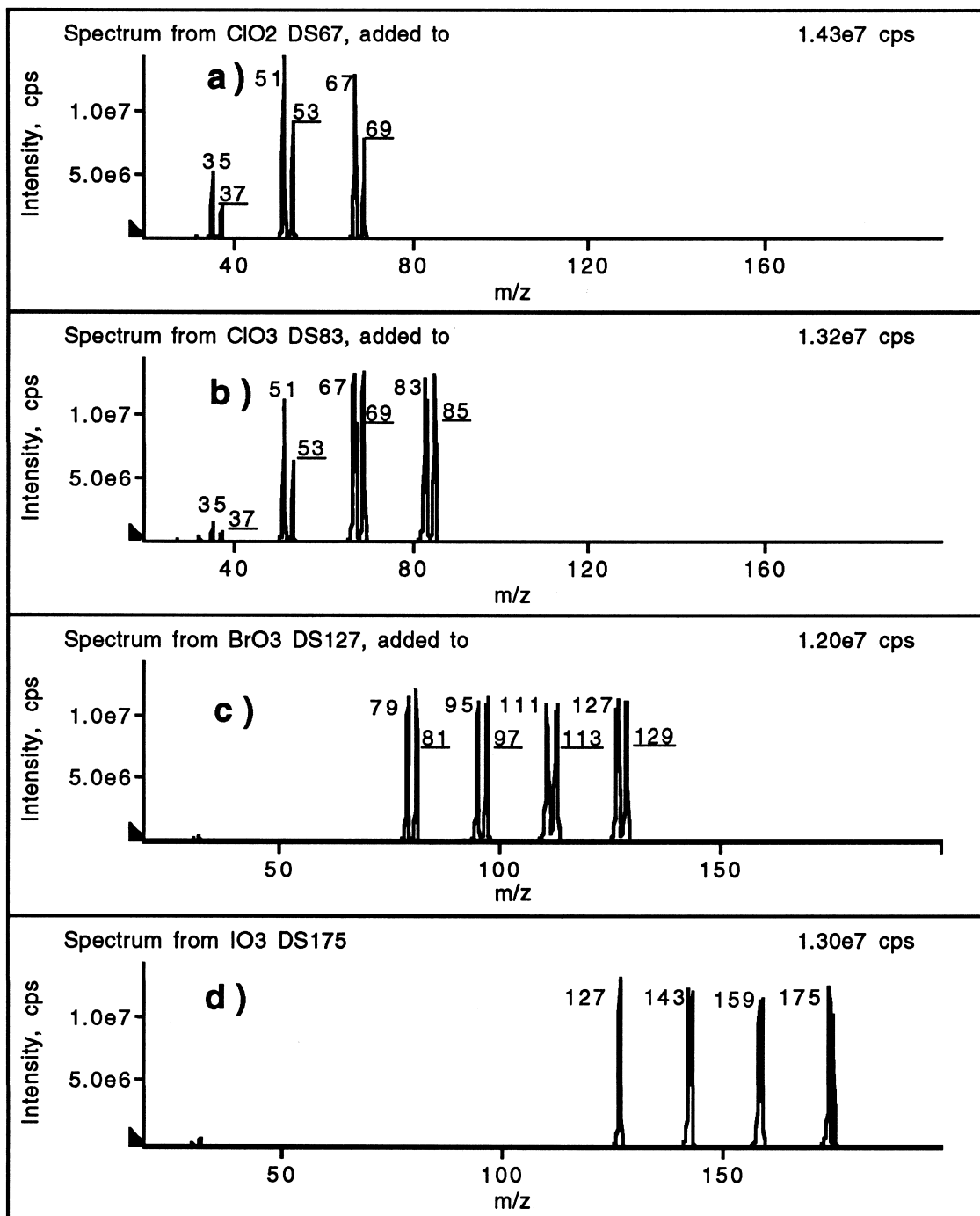
Fig. 1. Oxyhalide fragmentation spectra. The spectra were acquired in product scan mode with precursor ions (a) $^{37}ClO_2^-$ and $^{35}ClO_2^-$; (b) $^{37}ClO_3^-$ and $^{35}ClO_3^-$; (c) $^{81}BrO_3^-$ and $^{79}BrO_3^-$ and (d) $^{127}IO_3^-$.
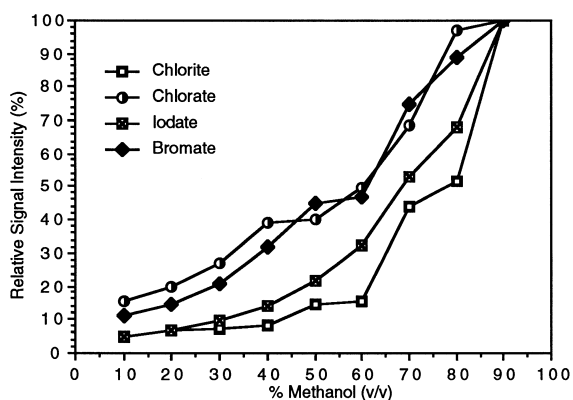
Fig. 2. Influence of methanol content in the mobile phase on oxyhalide sensitivity.

shown in Fig. 2. To avoid a 1:10 dilution of the sample with methanol, the alternative is solvent exchange, i.e. oxyhalide ions are extracted from the aqueous sample and redissolved in the water–methanol (10:90, v/v) eluent. Using anionic exchange properties, this solid-phase extraction (SPE) is performed with an AG9-SC column, the stationary phase being solvent compatible (SC). The optimal required solvent composition in the column effluent allows SPE on-line with IS-MS–MS detection. In this configuration, the solvent exchange step becomes a preconcentration step. The preconcentration volume was 5 ml.

As discussed in Section 1, classical IC eluents cannot be used for this coupling. Consequently, a new eluent system was developed for oxyhalide chromatography. When used as a concentrator, AG9-SC column performance is limited by ion-exchange competition: The column resin can trap only a certain quantity of analyte. Once the column capacity is exceeded, the trapping will not be quantitative. The processes become more complicated when ions have widely different affinities for the resin. If an anion has a high affinity for the resin and is present in much higher concentration, it can cause complete displacement of the analyte of interest, i.e. it acts as an eluent. Amongst anions that are usually strongly retained on the stationary phase, nitrate (NO_3^-) was shown to be the most suitable for oxyhalide analysis with IS-MS–MS [13]. Nitrate was introduced into the water–methanol eluent as ammonium nitrate, because the volatility of ammonium is well suited for

ionspray coupling. Fig. 3 shows a chromatogram of an oxyhalide standard mixture in deionized water, using a water–methanol (10:90 v/v) eluent containing 50 mg/l NO_3^-. It can be seen that, as described elsewhere [14], the presence of methanol in the eluent modifies the retention characteristics of the column, with chlorite eluting before iodate.

A water–methanol (10:90, v/v) eluent containing 50 mg/l NO_3^- was shown to be suitable for oxyhalide analysis with IC–IS-MS–MS, in terms of chromatographic separation as well as in terms of detection sensitivity.

3.3. Ion chromatography

In this study, the AG9-SC column was used both for SPE, sample preconcentration and analyte chromatography. After each analytical run, nitrate from the eluent was flushed from the column using carbonate–hydrogencarbonate buffers. Being regenerated, the stationary phase was then conditioned in water–methanol (10:90, v/v). All of these steps are described in Table 1.

3.4. Sample pretreatment

The analytical working conditions involve sample pretreatment to eliminate ions that can disturb extraction/preconcentration or detection steps. The ions that are usually removed from the sample matrix when using an AG9-SC concentrator for oxyhalide trace analysis are bicarbonate (HCO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-). These ions have a high affinity towards the resin and are present at mg/l levels in most drinking waters. The desalting procedure was described by Joyce and Dhillon [10]. Sulfate removal is performed with the formation of a $BaSO_4$ precipitate after percolating the sample through a Ba cartridge. For consistent sulfate removal, a sample must have a sufficient amount of a divalent cation present to displace the divalent barium from the resin so that it can react with sulfate. In some cases, 100 μl of a magnesium chloride solution (0.5 M Mg^{2+}) is added to the initial sample. Chloride is suppressed from the sample by means of a Ag cartridge in which chloride precipitates as AgCl. Hydrogencarbonate ions are eliminated by sample acidification with a H car-
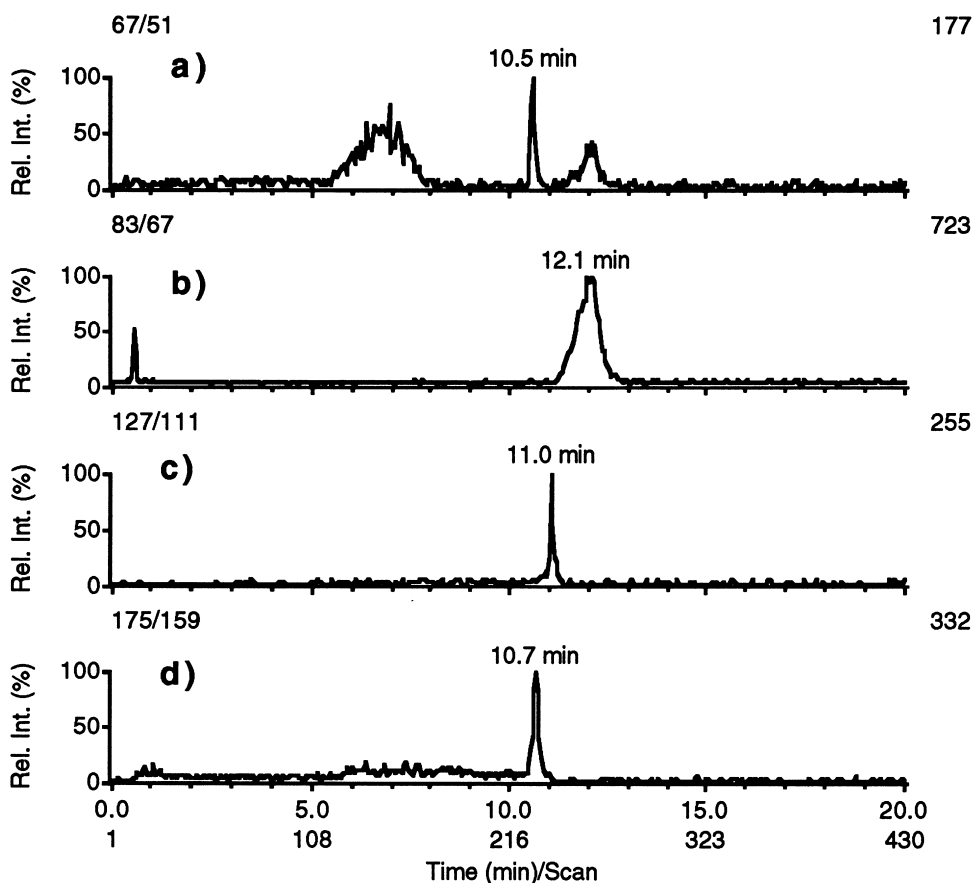
Fig. 3. Chromatograms of an oxyhalide standard mixture in deionized water. (a) Chlorite 67/51 (3.0 μg/l); (b) chlorate 83/67 (0.2 μg/l); (c) bromate 127/111 (0.2 μg/l) and (d) iodate 175/159 (2.0 μg/l).

tridge; the resulting dissolved carbon dioxide is eliminated by sparging with helium gas. The H cartridge is placed after the Ag cartridge, to trap any eluted silver ions, avoiding the accumulation of silver on the column. Oxyhalide recovery during pretreatment is usually high (>90%), but should be checked for each sample with multiple spiked additions.

3.5. Analytical results

In this analytical configuration, a very high sensitivity is reached for each compound. Limits of quantitation (LOQs), calculated as 10σ the blank, are 0.05 μg/l for bromate and chlorate, 0.50 μg/l for iodate and 1.00 μg/l for chlorite. Repeatability experiments were done at these LOQ levels and

results are reported in Table 3. It should be noted that LOQ determination and repeatability experiments were run with individual standard solutions because some salt, particularly sodium chlorite, was found to be contaminated with chlorate [13]. Linear working ranges were determined as 1–10 μg/l for

Table 3
Limits of quantitation (LOQs) of oxyhalide anions in water

	Selected transition	LOQ (μg/l)	SD (μg/l)	Accuracy (%)
ClO_2^-	67/51	1.0	0.1	1
ClO_3^-	83/67	0.05	0.01	1
BrO_3^-	127/111	0.05	0.01	4
IO_3^-	175/159	0.5	0.1	3

Repeatability experiment at LOQ level was done with $n=7$.
SD, standard deviation.

chlorite, 0.05–10.00 µg/l for chlorate, 0.05–1.00 µg/l for bromate and 0.5–10.0 µg/l for iodate. Simultaneous oxyhalide quantitation can be performed in many samples, such as mineral water or tap water [13].

The chlorite chromatogram (Fig. 3a) shows two unknown peaks at about 7 and 12 min. Only ions yielding the transition 67/51 should be seen with the MS operating in the MRM mode. Experiments have shown us that the first unknown peak disappeared using the strongest eluent (100 mg/l NO_3^-); this peak is a chlorite response and it seems that chlorite is not strongly retained on the stationary phase during the extraction/preconcentration step. However, the use of a high nitrate content eluent is not recommended because it can lead to coelution [13]. The second unknown peak is due to chlorate: In the spray, spontaneous fragmentation of analyte occurs and chlorate is present as ClO_3^- (mainly), ClO_2^-, ClO^- and Cl^-. Consequently, the contribution of ClO_2^- from chlorate is observed at the retention time for chlorate when recording the transition 67/51.

4. Conclusion

Coupling IC with IS-MS–MS is a very specific and sensitive technique for oxyhalide analysis. It allows the simultaneous identification and quantitation of oxyhalide at trace levels in disinfected drinking water. In particular, the toxicological threshold for bromate can be reached. This coupling is shown to be an attractive technique for inorganic species analysis.

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