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Determination of chlorate at low $\mu\text{g}/\text{l}$ levels by ion-chromatography with postcolumn reaction

Bernd Nowack, Urs von Gunten*

Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600 Dübendorf, Switzerland

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Abstract

A new method for the determination of low concentrations of chlorate in natural waters is described. Chlorate is analyzed by ion-chromatography followed by an osmate-catalyzed postcolumn reaction of chlorate with iodide and UV-detection of triiodide. The new osmate catalysis allows to carry out the oxidation of iodide by chlorate at pH 3 instead of 6 M HCl for the uncatalyzed reaction. A detection limit of 5 nM (0.4 $\mu\text{g}/\text{l}$) chlorate is achieved. The method also allows the simultaneous determination of chlorite, bromate, and nitrite at the low $\mu\text{g}/\text{l}$ level. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorate is a byproduct of drinking water disinfection and can be formed through several pathways: (i) Chlorine dioxide oxidizes the organic material under formation of chlorite, which can then be oxidized to chlorate by ozone [1] or hypochlorite [2] if combinations of chlorine dioxide and these disinfectants are used. (ii) Chlorate is a byproduct of chlorine dioxide generation [3] or (iii) can be present in commercial hypochlorite solutions [4,5]. Ozonation of waters with a (iv) chlorine residual [1] or (v) chlorine dioxide residual [6] also results in the formation of chlorate.

Both chlorite and chlorate have potential harmful effects [7]. The World Health Organization (WHO) proposed a guideline value of 200 $\mu\text{g}/\text{l}$ for chlorite but no value for chlorate due to limited knowledge

about its toxicity [8]. However, the WHO recommends to minimize the level of chlorate as much as possible as long as there is no reliable toxicological data. In Switzerland, the sum of chlorite and chlorate is limited to 300 $\mu\text{g}/\text{l}$ in drinking waters [9]. The new proposed tolerance limit in Switzerland is 200 $\mu\text{g}/\text{l}$ for each chlorite and chlorate [10].

Chlorate is generally measured by ion-chromatography with conductivity detection with a detection limit of 50 $\mu\text{g}/\text{l}$ [11] or by a flow injection system with a detection limit of about 100 $\mu\text{g}/\text{l}$ [12,13]. Therefore, the need for a more sensitive method is given.

Recently, ion-chromatography followed by post-column reactions with bromide [14] and iodide [15,16] have been described for the analysis of the oxyhalides iodate, bromate, and chlorite. The oxidation of iodide by the oxyhalide leads to iodine (I_2) which further reacts to triiodide (I_3^-) in excess of iodide. Triiodide has a very high molar absorptivity of 38 200 l/mol/cm at 288 nm [15]. The two

*Corresponding author. +41-1-823-5270; fax: +41-1-823-5028.
E-mail address: vungunten@eawag.ch (U. von Gunten)

methods are able to detect the oxyhalides in drinking water at concentrations down to 0.1 $\mu\text{g}/\text{l}$.

Chlorate, however, cannot be measured by these methods due to its very low reactivity towards iodide. Concentrated acid solutions (6 M HCl) are required for a rapid oxidation of iodide by chlorate. Such conditions are not suitable for conventional postcolumn systems.

It has been known for a long time that osmium tetroxide (OsO_4) catalyzes the oxidation of iodide by chlorate [17]. OsO_4 has also been used as a catalyst for the arsenometric titration of chlorite [18]. We have tested OsO_4 for its suitability as postcolumn catalyst and have developed conditions under which chlorate oxidizes iodide to iodine at pH 3 with a sufficient rate. The present study describes the conditions and a setup for the use of this reaction to detect chlorate in natural waters at low $\mu\text{g}/\text{l}$ levels.

2. Experimental section

2.1. Materials

The diagram in Fig. 1 illustrates the general layout of the method. After a conventional ion-chromatography set-up with HPLC pump (Sykam S1000, Gauting, Germany), analytical column and suppressor, the postcolumn reagent containing iodide and osmate is added. A 750 μl reaction coil is followed by a UV-Vis detector where the signal is detected at 288 nm.

A Dionex AS9HC column with a AG9HC guard column was used for separation. The eluent was

acidified by a ASRS-1 membrane exchange suppressor (Dionex) run in the chemical suppression mode. The postcolumn reagent was supplied by a Dionex PC10 Reagent Delivery Module via a KEL-F mixing tee. UV-Vis detection was performed by a Spectroflow 773 absorbance detector (Kratos, Ramsey, NJ). The eluent and the postcolumn reagent were kept under a helium atmosphere. Details of the composition of the eluent and the postcolumn reagent are given in Table 1.

The H_2O_2 cleaning is injected into the system between the suppressor and the mixing tee. 2–3 ml are sufficient for complete removal of the Os^{V} precipitate.

2.2. Reagents

All reagents used were purchased from Fluka (Buchs, Switzerland). It is important to use highest grade KI (Fluka puriss. p.a.) [15]. OsO_4 was obtained as a 4% solution (Fluka) in a sealed glass vial. **Caution:** OsO_4 is volatile and poisonous and should be handled with care. The reduction of OsO_4 to osmate was conducted in a well ventilated fume hood by adding 0.26 ml 4% OsO_4 to a basic solution (5 mM NaOH) of 380 ml 0.1 M KI and 20 ml ethanol. After reduction to osmate, the osmium is no longer volatile and no extra safety precautions have to be used. The yellow color that develops rapidly fades to give a clear solution of osmate. This solution should be prepared at least 24 h before use. It was found that fresh solutions caused more precipitation of Os^{V} in the reaction coil than aged solutions. The osmate solution is stable for several

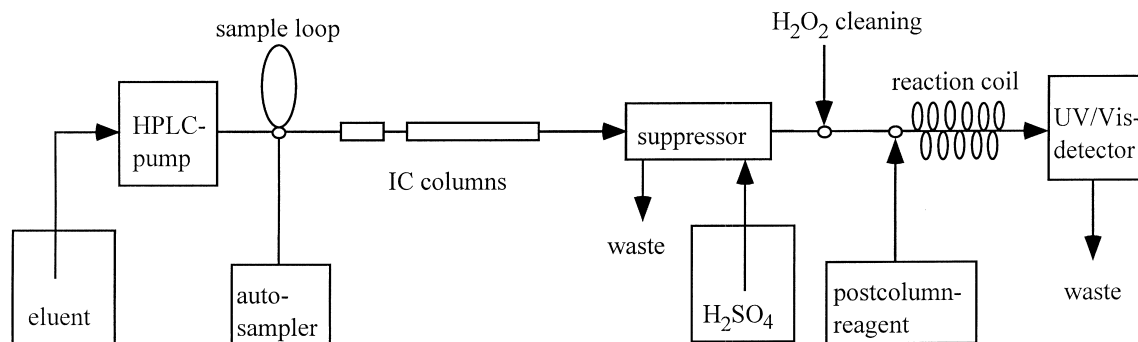


Fig. 1. Scheme of the instrumental setup for the ion-chromatographic analysis of chlorate.

Table 1
General conditions

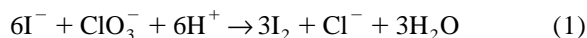
<i>Postcolumn reaction</i>	
Reagent	0.1 M KI/0.1 mM OsO ₄ /5 mM NaOH/5% ethanol
Reagent flow-rate	0.2 ml/min
Reaction coil	750 μl
Reaction temperature	room temperature
UV detector cell	
Volume	12 μl
Path length	8 mm
Wavelength	288 nm
<i>Ion-chromatography</i>	
Guard column	AG9HC (Dionex)
Analytical column	AS9HC (Dionex)
Eluent	50 mM sodium tetraborate decahydrate/6 mM sodium formate
Flow-rate	1 ml/min
Suppressor	ASRS-1 (Dionex)
Regenerent	45 mM H ₂ SO ₄
Regenerent flow-rate	3 ml/min
Sample loop	750 μl
Run time	20 min
Cleaning solution	2–3 ml 0.1 M H ₂ O ₂

weeks. The high pH of above 11.5 in the reagent prevents the iodide to get oxidized by oxygen or osmate.

3. Results and discussion

3.1. Chemistry of the postcolumn reaction

Chlorate is able to oxidize iodide to iodine at pH below 0 according to Eq. (1)



Iodine then reacts with excess iodide to form the triiodide I₃⁻ (Eq. (2)), which can be detected at 288 or 352 nm. The oxidation of iodide by chlorate can be catalyzed by low concentrations of OsO₄ [17]. Fig. 2 (lower curve) shows the reaction of 4 μM NaClO₃ in 0.02 M KI catalyzed by 20 μM OsO₄ at pH 2.0. The reaction was followed by measuring the absorption of the triiodide at 288 nm. It can be seen that the reaction is autocatalytic at such low chlorate concentrations. After 1 min, only about 10% of

chlorate have reacted. Lowering the pH increased not only the reaction rate but also the blank reaction of OsO₄ with iodide. OsO₄ is therefore not a suitable catalyst for a postcolumn reaction where a maximum reaction time of about 1 min is given. We have found, however, that the reduced form of OsO₄, the osmate ion (OsO₄²⁻), could catalyze the reaction of chlorate with iodide with a very high initial rate. OsO₄ can be reduced to osmate with ethanol at high pH [19]. The upper curve in Fig. 2 shows the oxidation of iodide by chlorate catalyzed by osmate for the same conditions as for the experiment with OsO₄. The reaction was complete after about 1 min and therefore lies within the time frame for post-column reactions. Due to the mild conditions it is suitable for conventional postcolumn systems. An optimum pH range was found to be 3–3.5, where the reaction of chlorate with iodide was fast but the blank reaction of iodide with oxygen slow. The eluent consists of a basic borate solution and has to be acidified after the analytical column. We have used a membrane suppressor (Dionex ASRS-1) in the chemical suppression mode for acidification. Suppression of a 50 mM sodium borate solution results in a pH of 5.3. In order to achieve a pH of 3.3 after the analytical column, 6 mM sodium in the

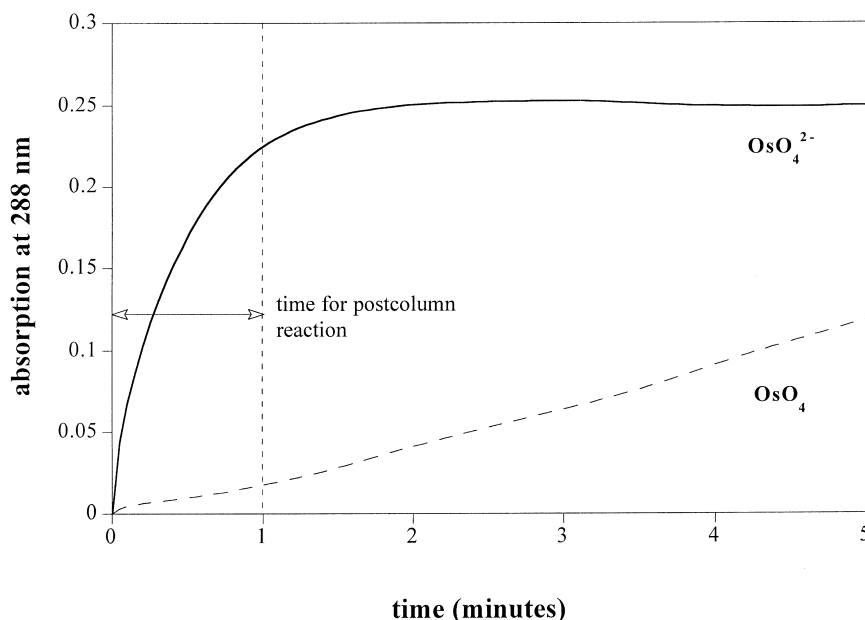


Fig. 2. Oxidation of 0.02 M iodide by 4 μM chlorate catalyzed by 20 μM OsO_4 or OsO_4^{2-} (osmate) at pH 2. The reaction was followed by measuring the absorption of the triiodide at 288 nm.

form of sodium formate was added to the eluent. Sodium is exchanged against H^+ in the suppressor and after addition of the basic iodide–osmate solution an optimum pH of 3.3 is achieved.

3.2. System performance

An acidic solution of osmate (Os^{VI}) slowly disproportionates to Os^{VII} , which is soluble, and Os^{V} , a black precipitate [19]. With time, a black precipitate can be observed in the reaction coil, accompanied by an increase of the background absorption and a decrease of the response of the chlorate signal. The precipitate can be removed by purging a few millilitres of a 0.1 M H_2O_2 solution through the whole system after the suppressor (see Fig. 1). All tubing from the mixing tee to the reaction coil and the UV cell are cleaned by this procedure. The black precipitate dissolves instantaneously in the presence of H_2O_2 . This cleaning step is repeated after a operation time of about 8 h (25 injection with 20 min run time).

3.3. Eluent and postcolumn reagent

In distilled water the use of a standard carbonate eluent is possible for the analysis of chlorate by the osmate catalyzed reaction described here. Samples of natural waters, however, analyzed with the carbonate eluent exhibit an interference with the postcolumn reaction. A dip in the baseline was observed at the same retention time where chlorite elutes. A borate eluent eliminates this problem and was therefore used for all analyses. The concentration of iodide in the postcolumn reagent was used as described in Ref. [15]. The flow-rate of the postcolumn reagent was optimized so that formation of the black Os^{V} precipitate was minimized. A flow-rate of 0.5 ml/min resulted in a very rapid blackening of the reaction coil. Reduction of the flow to 0.2 ml/min eliminated this problem to a great extent. Upon starting the postcolumn reagent, the background absorption achieves a constant value after a few minutes. The peak area of a chlorate standard remained constant over 25 injections. Afterwards, the peak area decreased slowly (0.9% per injection over the next 15

injections), accompanied by an increase in the background absorption. Cleaning of the system by H_2O_2 as described in the Section 2 restores the system to the initial state.

3.4. Calibration and detection limits

A plot of the peak area versus the concentration of chlorate is linear in the range from 0.01 to 10 μM with correlation coefficients r^2 of 0.998 in the 0.01–0.1 μM (0.8–8 $\mu\text{g/l}$) and r^2 of 0.999 in the 1–10 μM (8–80 $\mu\text{g/l}$) range. Fig. 3 shows chromatograms of 0.01 to 0.1 μM (0.8–8 $\mu\text{g/l}$) chlorate in distilled water with the corresponding calibration graph. The relative standard deviation of the peak area of 1 μM (80 $\mu\text{g/l}$) chlorate was 2.4% ($n=7$), of 0.1 μM (8 $\mu\text{g/l}$) 4.9% ($n=7$) and of 0.02 μM (1.7 $\mu\text{g/l}$) 10.6% ($n=8$). The detection limit is 0.005 μM (0.4 $\mu\text{g/l}$)

chlorate ($S/N=3$). The recovery of 0.1 μM (8 $\mu\text{g/l}$) chlorate in a drinking water was 103% with a standard deviation of 5.5% ($n=6$).

3.5. Simultaneous determination of chlorite, bromate, and nitrite

The method allows not only the determination of chlorate but also of chlorite, bromate, and nitrite. Fig. 4 shows a chromatogram of the three oxyhalides and nitrite at concentrations of 0.4 μM chlorite and chlorate (27 and 33 $\mu\text{g/l}$), 0.2 μM bromate (26 $\mu\text{g/l}$), and 2 μM nitrite (92 $\mu\text{g/l}$) added to a tap water containing chloride (10 mg/l), nitrate (6.5 mg/l), and sulfate (24 mg/l). Iodate cannot be detected at low concentrations due to system peaks at the same retention time (about 5 min). Methods for trace analysis of iodate using other postcolumn

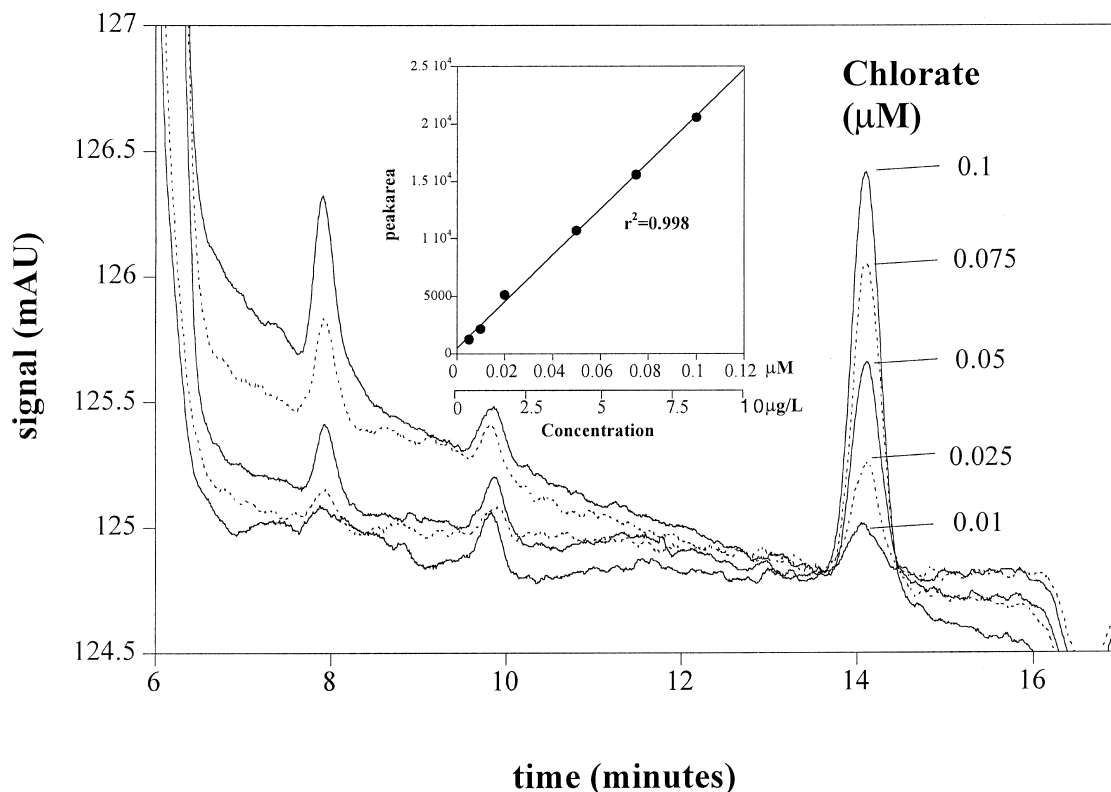


Fig. 3. Chromatograms of 0.01–0.1 μM (0.8–8 $\mu\text{g/l}$) chlorate in distilled water. The inset shows the plot of peak area versus concentration for these samples.

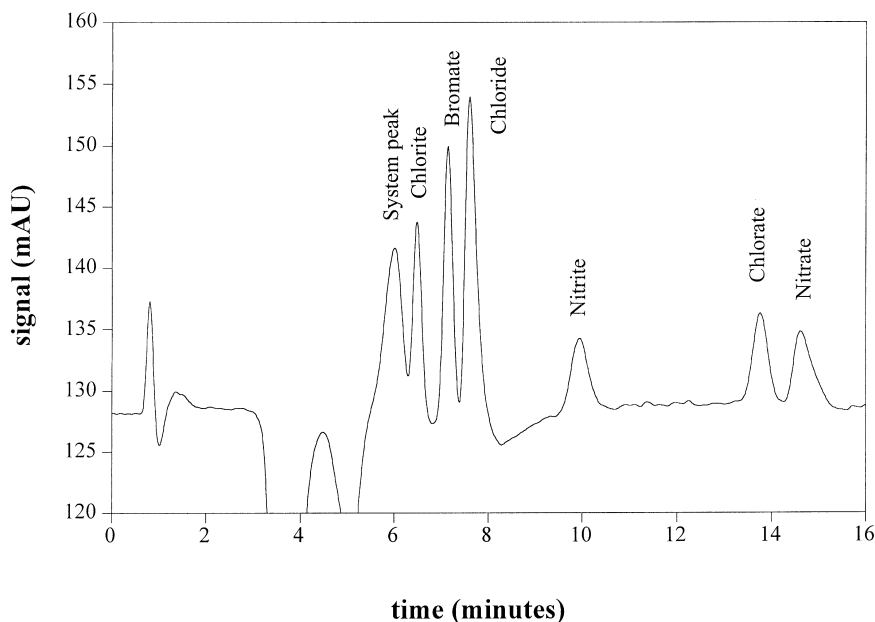


Fig. 4. Chromatogram of $0.4 \mu\text{M}$ chlorite and chlorate (27 and $33 \mu\text{g/l}$), $0.2 \mu\text{M}$ bromate ($26 \mu\text{g/l}$) and $2 \mu\text{M}$ nitrite ($92 \mu\text{g/l}$) in tap water (Dübendorf, Switzerland), containing 10 mg/l chloride and 6.5 mg/l nitrate.

reagents have been described [15,16]. The calibration graph for chlorite is linear down to a concentration of $0.05 \mu\text{M}$ ($3 \mu\text{g/l}$), for bromate to $0.01 \mu\text{M}$ ($1 \mu\text{g/l}$), and for nitrite to $1 \mu\text{M}$ ($46 \mu\text{g/l}$).

3.6. Interferences

The anions chloride, phosphate, nitrate, and sulfate also accelerate the osmate catalyzed oxidation of iodide to iodine. The response of nitrate is about 400-times lower than for chlorate. With 10 mg/l nitrate ($160 \mu\text{M}$) and $0.4 \mu\text{M}$ chlorate, the ratio of the peak areas of chlorate to nitrate is 0.98. For a conductivity detection of the same sample, the ratio of the peak areas is $1.5 \cdot 10^{-3}$. For concentrations of nitrate typically encountered in drinking waters only small peaks appear in the chromatogram. In the previously described iodate, bromate, and chlorite analysis by a molybdate-catalyzed oxidation of iodide, the matrix anions do not interfere at all at concentrations between 100 and 1000 mg/l [16]. The chlorate method described here is therefore not as robust as this method. However, as shown in Fig. 4 (addition of oxyhalides to tap water containing 10 mg/l chloride, 6.5 mg/l nitrate and 24 mg/l sulfate),

the chlorate peak is well separated from the nitrate peak using the AS9HC column. Chloride at concentrations of up to 100 mg/l does not interfere with the analysis of chlorite, bromate, and nitrite. A 40 mg/l concentration of nitrate does not interfere with the determination of chlorate.

3.7. Application to treated waters

Water samples from a drinking water treatment plant of Zürich (Switzerland) have been analyzed using the new method. River water (1.5 mg/l DOC, $15 \mu\text{g/l}$ ammonia, 2 mM bicarbonate, pH 8) is oxidized in a first treatment step with a mixture of 0.14 mg/l ClO_2 and 0.46 mg/l Cl_2 . Fig. 5 depicts a chromatogram of this treated water, sampled 5 min after addition of the disinfectants. The chlorite and chlorate peak are clearly visible and are well separated from chloride (about 3 mg/l) and nitrate (about 2 mg/l). Nitrite ($10 \mu\text{M}$) was added to quench free chlorine and ClO_2 . Upon reaction with nitrite, ClO_2 forms chlorite which has to be subtracted from the total measured chlorite by also measuring ClO_2 independently. The concentrations of chlorite and

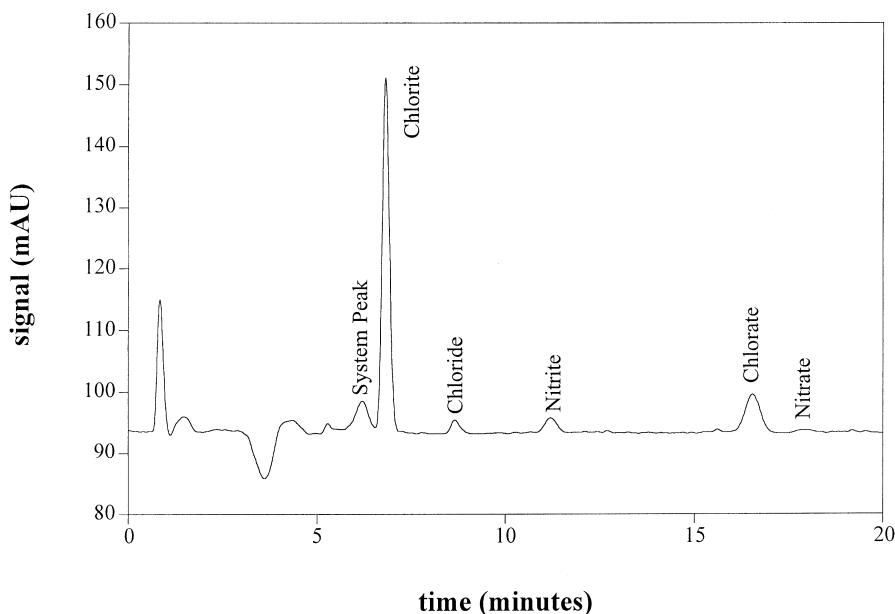


Fig. 5. Chromatogram of a river water oxidized with 0.14 mg/l ClO_2 /0.46 mg/l Cl_2 from a drinking water treatment plant of Zürich, Switzerland. Nitrite was added to quench free chlorine and chlorine dioxide. The concentration of chlorite is 1.06 μM (71 $\mu\text{g/l}$) and of chlorate 0.42 μM (35 $\mu\text{g/l}$).

chlorate, determined by external calibration are 1.06 μM (71 $\mu\text{g/l}$) and 0.42 μM (35 $\mu\text{g/l}$), respectively.

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