

APPLICATION OF ION CHROMATOGRAPHY FOR DETERMINATION OF OXYHALIDES ANIONS IN WATER

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ZASTOSOWANIE CHROMATOGRAFII JONOWEJ DO OZNACZANIA UTLENIONYCH HALOGENOPOCHODNYCH W WODACH

Dezynfekcja wód do picia była dotychczas przeprowadzana za pomocą chlorowania. Jest to dobrze znana, efektywna metoda mająca wiele zalet, niemniej podczas tego procesu tworzą się niebezpieczne dla zdrowia produkty uboczne takie jak trihalometany czy chloryny, chlorany i bromiany.

Innym procesem dezynfekcji pojawiającym się jako obiecująca alternatywa wobec chlorowania jest ozonowanie. Pomimo niezaprzeczalnych zalet, pojawiają się tam również nieokreślone do końca niebezpieczeństwa. Dotyczą one szczególnie tworzenia się kancerogennych anionów bromianowych w wodach zawierających bromki. Oznaczanie bromianów i innych nieorganicznych halogenopochodnych jest zazwyczaj przeprowadzane za pomocą chromatografii jonowej z detekcją konduktometryczną.

Poprawę dokładności oznaczania można osiągnąć poprzez stosowanie alternatywnych technik łączonych takich jak IC-ICP-MS czy IS-MS-MS. Techniki te są wprawdzie bardzo czułe, lecz są również bardzo wyrafinowane i drogie. Inną alternatywą, relatywnie tanią i dobrą propozycją są tzw. techniki "reakcji po kolumnie", czyli metody derywatyzacyjne połączone z chromatografią jonową.

Niniejsza praca stanowi przegląd najnowszych osiągnięć w dziedzinie technik analitycznych stosowanych w oznaczaniu nieorganicznych halogenopochodnych produktów dezynfekcji wód do picia.

S u m m a r y

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

Another disinfection process, which has emerged as the most promising alternative to chlorination technique, is ozonation. In spite of undeniable advantages, there are certain undefined hazards resulting from this method of water treatment. It is especially due to formation of carcinogen bromate anions in bromide containing waters. Determination of bromate as well as other inorganic oxyhalides is usually carried out by ion chromatography with conductivity detection.

The detection sensitivity can be improved by using alternative hyphenated techniques such as IC-ICP-MS or IS-MS-MS. These techniques are very sensitive, but are highly sophisticated and the instrumentation is very expensive. "Post-column reactions", i.e. derivative techniques coupled with ion chromatography are a relatively cheap and good alternative.

This paper is a review of the newest achievements in analytical techniques used for determination of inorganic oxyhalides by-products formed during various drinking water disinfection processes.

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 in addition, are biologically impure. It is therefore a necessity to purify and disinfect source waters in order to obtain waters of a drinking quality.

Disinfection of source waters is in practice performed by chlorination or ozonation procedure [3, 4, 10, 42, 48]. During the 1970s it was discovered that chlorination of drinking water produced carcinogens, such as trihalomethanes, haloacetic acids and others [6, 7, 9, 20, 23, 24, 47, 52]. Chlorite (ClO_2) and chlorate (ClO_3^-) are the disinfection by-products (DBPs) formed when chlorine dioxide (ClO_2) is used to disinfect drinking water [27, 65]. 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. Ozonation has emerged as one of the most promising alternatives to chlorination [40].

During the last decade, the use of ozone in the treatment of drinking water to improve taste, odor, organic and inorganic micropollutants has been spreading [35].

The disinfection of bromide-containing source waters results in generation 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 [22, 53]. Bromates are possible human carcinogen [26, 38]. Studies have indicated that the concentrations of bromate in processed waters are dependent on several parameters including ozone dose and duration, temperature, pH and indigenous concentration of bromide [5, 37]. The maximum contamination level (MCL) of bromate in drinking water, as recommended by World Health Organization (WHO), European Countries (EC) as well as in Poland is $10 \mu\text{g}/\text{dm}^3$ [15, 25, 49].

The MCL 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.

IARC classified bromate in group B-2 (as "probable human carcinogen") and established a drinking water maximum contaminant level goal (MCLG) of zero and MCL of $10 \mu\text{g}/\text{dm}^3$ for bromate in finished drinking water [31]. 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 reason 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 [29, 57, 64]. 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 [54].

Ion chromatographic methods with direct injection and conductivity detection after chemical suppression have been published by Jackson et al. [33]. Under idealized conditions MDL for bromate, chlorite and chlorate are $1.73 \mu\text{g}/\text{dm}^3$; $2.38 \mu\text{g}/\text{dm}^3$ and $1.07 \mu\text{g}/\text{dm}^3$, respectively. A direct injection ion chromatographic method using an anion-exchange column with a carbonate eluent and suppressed conductivity detection can be used for the determination of these disinfection by-products anions and bromide at low $\mu\text{g}/\text{dm}^3$ levels [34]. No additional sample pretreatment, other than filtration is required. The

method is linear for the oxyhalides and bromide over the typical concentration range expected for these analyses in drinking water and quantitative recoveries were obtained for drinking water samples spiked at $10 \mu\text{g}/\text{dm}^3$.

By using a high-capacity anion-exchange column it should be possible to determine bromate at a level lower than $1 \mu\text{g}/\text{dm}^3$ by direct injection of a very large volume (up to 1 cm^3) without any sample preconcentration or pretreatment [14]. The experimental results showed that matrix effect, due to inorganic ions contained in drinking water, strongly influenced the chromatographic behavior of bromate peak. The increase of the total ion content led to a correlated decrease in the efficiency of the analyte peak so that effective detection limits depended on the matrix composition. In this work chromatographic parameters such as efficiency, asymmetry and resolution of bromate peak are discussed in relation to the concentration of the main inorganic anions and the injection volume.

An automatic flow injection analysis (FIA) has been reported by Gordon et al. [28]. This sensitive ($1 \mu\text{g}/\text{dm}^3$) method utilizes the oxidation of chlorpromazine by bromate but is distributed by other disinfection by-products like chlorite when these interfering ions are not removed prior to analysis.

These techniques suffer from the existence of interference that require time consuming step for elimination, clean up and separation before the instrumental measurements [56, 61].

Much lower detection limits are obtained using hyphenated techniques as ion chromatography coupled with mass spectrometry (IC-MS) [8, 12, 36]. In one of the first studies, Creed et al. [17] reported a detection limit of $0.1 - 0.2 \mu\text{g}/\text{dm}^3$ after utilizing a Dionex AG10 column for sample preconcentration. The new approach that permitted ultratrace determinations of bromate in drinking waters, the main benefits being low limit of detection ($0.13 \mu\text{g}/\text{dm}^3$ based on $500 \cdot 10^{-6} \text{ m}^3$ sample injection), rapid analysis time (10 min/sample), and good precision (2.8% at the $5 \mu\text{g}/\text{dm}^3$ level) was reported by Elwaer et al. [21].

The ICP-MS detection for the simultaneous determination of halogen and oxyhalogen anions as sulfate, phosphate, selenite, selenate and arsenate was described by Divjak et al. [19]. The limits of detection ($S/N = 3$, sample injection volume $50 \cdot 10^{-6} \text{ m}^3$) obtained with the IC-ICP-MS after the optimization were $0.67 \mu\text{g}/\text{dm}^3$ for BrO_3^- ; $0.47 \mu\text{g}/\text{dm}^3$ for Br^- ; $69 \mu\text{g}/\text{dm}^3$ for ClO_2^- ; $4 \mu\text{g}/\text{dm}^3$ for Cl^- ; $47 \mu\text{g}/\text{dm}^3$ for ClO_3^- ; $13 \mu\text{g}/\text{dm}^3$ for SO_4^{2-} ; $36 \mu\text{g}/\text{dm}^3$ for PO_4^{3-} ; $0.4 \mu\text{g}/\text{dm}^3$ for SeO_3^{2-} ; $0.3 \mu\text{g}/\text{dm}^3$ for SeO_4^{2-} and $0.4 \mu\text{g}/\text{dm}^3$ for AsO_4^{3-} .

Several authors [16, 44, 50] investigated another on-line IC-ICP-MS systems. Yamanaka et al. [66] described a specific determination for bromate, iodate and other halogen anions in drinking water by using this technique with postcolumn derivatization. The advantages of ICP-MS as an element of selective detector were evaluated for bromate and iodate by considering the comparison with the postcolumn derivatization.

A sensitive method for analyzing chlorite, chlorate, bromate and iodate in water by ion chromatography coupled with ionspray tandem mass spectrometry (IS-MS-MS) has been developed by Charles and Pepin [11]. Prior to the analysis, the samples were subjected to off-line sample clean up with Ba, Ag and H form resins to remove sulfate, chloride and

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 single run with very high specificity and sensitivity.

The application of atmospheric pressure ionization mass spectrometry (API-MS), coupled with IC, showed a performance comparable to that of IC-MS/MS and IC-ICP-MS [2, 51]. Diemer and Heumann [18] reported a detection limit in the range of 0.03–0.07 $\mu\text{g}/\text{dm}^3$ with an anion-exchange chromatography coupled with negative thermal ionization isotope dilution mass spectrometry (NTI-IDMS). The detection of bromate in ozonated water by IC-ICP-MS does not suffer from chloride interference associated with IC conductivity detection but tribromoacetic acid must be removed before analysis.

A speciation method utilizing IC-ICP-MS is described by Panssar-Kallio and Manninen [45] for simultaneous analysis of eight halogenides and oxyhalogens: chloride, chlorite, chlorate, perchlorate, bromide, bromate, iodide and iodate. Chloride and chlorate were the chlorine species found in these water samples, and iodine exists as both iodate and iodide. In the case of bromine species conversion had taken place, since total bromine concentrations were increased during disinfection, but bromide concentrations were decreased.

These techniques are very sensitive and single analysis is cheap, but is highly sophisticated, and the instrumentation is very 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 simultaneous determination of inorganic disinfection by-products is IC coupled with a post-column reaction (PCR) followed by spectrometric detection [62, 63]. Chiu et al. [13] reported a simple and rapid spectrometry, which was based on the strong absorption of the tribromide, converted from bromide under an excess of hydrobromic acid. The same procedure was used to determine bromate by using IC with post column reaction [32, 41]. Using the on-line hydrobromic acid generator employing a cation exchange hollow fiber these were performed a high precision determination of bromate. Under optimized conditions, the performance for bromate determination was obtained as given below. The detection limit for a bromate injection of 0.1 cm^3 was 0.35 $\mu\text{g}/\text{dm}^3$. The linear range was over 4 orders of magnitude, from 0.5 $\mu\text{g}/\text{dm}^3$ to 10 mg/dm^3 . The relative standard deviation (RSD) for 1 $\mu\text{g}/\text{dm}^3$ of bromate solution was 4.6% ($n = 10$). The post-column derivatization system combined with suppressed conductometric detection can be applied to the simultaneous determination of bromate and common anions as fluoride, chloride, nitrite, bromide, phosphate, sulfate and nitrate in drinking water.

PCR method based on o-dianiside was developed by Warner et al. [58]. The limit of detection of bromate in this method is 1 $\mu\text{g}/\text{dm}^3$, however these are some disadvantages: poor resolution of bromate and chlorite ions and carcinogenic characteristic of o-dianisidine.

Chlorate oxidizes the iodide into iodine, which reacts, with excess iodide to give the triiodide that is detectable at 288 nm. This method was published by Nowack and Gunten [43]. The method also enables the simultaneous determination of chlorite, bromate and nitrite at the low $\mu\text{g}/\text{dm}^3$ level.

Determination of bromate by using fuchsin as post-column reagent with MDLs 0.1 $\mu\text{g}/\text{dm}^3$ level was described by Achilli and Romele [1]. In July 1997, the US Environmental Protection Agency (US EPA) began sampling and analyzed water matrices from US municipalities serving population greater than 100 000 for low-level bromate ($>20 \mu\text{g}/\text{dm}^3$) in support of the Information Collection Rule (ICR).

mental Protection Agency (US EPA) began sampling and analyzed water matrices from US municipalities serving population greater than 100 000 for low-level bromate ($>20 \mu\text{g}/\text{dm}^3$) in support of the Information Collection Rule (ICR).

US EPA has reported two methods capable of detecting bromate at or below promulgated MCL level $10.0 \mu\text{g}/\text{dm}^3$. These methods published in the end of 1997, are EPA Method 300.1 and 317.0 [30, 46], which reduced the Method 300.0 bromate method detection limit from $20.0 \mu\text{g}/\text{dm}^3$ to $1.4 \mu\text{g}/\text{dm}^3$ 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 new postcolumn reagent method with o-dianisidine [55].

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.

International Standard Organization (ISO) published in 1997 a method for determination of chlorate, chloride and chlorite in water with low contamination by using ion chromatography [59]. 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/CD method [39].

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 15061 Method in 2001 [60].

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