

A Flow Method with Spectrophotometric Detection for Determination of Chlorite Ions in Drinking Water

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The paper presents a newly developed flow method with spectrophotometric detection for determination of chlorites in drinking water. The method is based on reaction of chlorite ions with iron(II) in an acidic environment. The analytical signal was measured for the coloured Fe(II)/o-phenanthroline complex at 512 nm. Determinations were carried out using a flow system. Validation studies revealed that the method is linear in the analyte's concentration range 0.1–6.0 mg L⁻¹ and assures determination precision RSD < 0.40%. Limit of detection and limit of quantification were estimated as 0.01 and 0.03 mg L⁻¹, respectively. The interferences caused by different ions were studied taking into consideration their concentrations ranges occurring in water classified into four quality classes. The method was applied to the analysis of water samples taken from different intakes in Kraków (Poland) and the analytical results were compared with those obtained by ion chromatography method.

W pracy przedstawiono metodę przeplywową z detekcją spektrofotometryczną do oznaczania chloranów(III) w wodzie pitnej. Podstawą metody jest reakcja jonów chloranowych(III) z jonami Fe(II) w środowisku kwaśnym i pomiar sygnału analitycznego dla barwnego kompleksu jonów Fe(II) z o-fenantroliną przy długości fali 512 nm. Oznaczenia wykonywano przy użyciu zestawu do analizy przeplywowej. Badania walidacyjne wykazały, że metoda charakteryzuje się liniowością w zakresie stężenia 0.1–6.0 mg L⁻¹ pozwalając na oznaczenia analitu z precyzją (RSD) < 0.40%. Granice wykrywalności i oznaczalności analitu wynosiły

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odpowiednio 0.01 i 0.03 mg L⁻¹. Zbadano interferencje wywołane występowaniem różnych jonów w zakresach stężeń typowych dla wód o czterech klasach czystości. Metodę zastosowano do analizy próbek wód pobranych z różnych ujęć na terenie Krakowa. Otrzymane wyniki analityczne porównano z rezultatami otrzymanymi metodą chromatografii jonowej.

Drinking water quality is an important parameter strictly controlled by several institutions. The European Commission lays down the requirements for the drinking water quality in the Directives of the European Union Council [1]. The World Health Organization (WHO) publishes a special document concerning drinking water quality [2], which reports on the recommendations regarding analytical methods for water quality assessment as well as gives the allowable values of different parameters of drinking water and the basis, on which they have been determined.

Water treatment plants are responsible for providing consumers with water of sufficient quality. Their task is to destroy pathogenic organisms present in water or suppress their activity to the maximum possible extent [3], as well as to control water quality in terms of its organoleptic characteristics. At present, owing to the progress in science and technology, the use of such agents as chlorine, ozone, chloramines or iodine for water treatment is limited, mainly due to the harmful effects of the by-products generated in their reactions with water.

The World Health Organization recommends using chlorine dioxide for water treatment purposes [2]. This agent is effective owing to its strong oxidizing properties as well as good antiviral and antibacterial activity. An additional advantage of this agent is that it allows obtaining water of better organoleptic properties [2, 3]. Unfortunately, the products of water treatment with ClO₂ are health-threatening:



According to the current research, chlorite ions are more harmful to health. It has been evidenced that they are produced together with chlorate ions, and their presence in drinking water at the level of 1.2 mg L⁻¹ can pose a threat to the human health. Severe effects are experienced upon exposure to the concentration of 1000–15 000 mg L⁻¹ ClO₂⁻ [4]. Nevertheless, WHO supports this water treatment method and points out that chlorite and chlorate ions are less harmful compared to the by-products formed when water is treated using other methods. It is also emphasized that the presence of chlorite ions in water is temporary. In cases of substantial water pollution, *e.g.* during a flood, WHO allows exceeding the 0.70 mg L⁻¹ concentration level of chlorites.

The official analytical method for determination of chlorites in water is ion chromatography [5–7]. It is recommended by a number of institutions, including the European Environmental Protection Agency (EPA) [8]. However, this method is relatively low-productive, very time-consuming (a single analytical result is obtained after

approx. 25 min), and expensive in terms of both instrumentation and operation. Considering the above, novel alternative analytical approaches have been recently proposed; they utilize capillary electrophoresis [9], UV spectrophotometry [10] and colorimetry [11].

The literature provides a few suggestions concerning the use of flow injection systems for determination of chlorites in water samples. Ohura [12] utilized a complex system to perform multi-stage analysis with potentiometric detection. The complicated measurement system with an ion-exchange column and two detectors as well as long time required for a single measurement (increased to several minutes) reduces the applicability of this method in the routine analyses. Miller [13] used the iodine-metric method with spectrophotometric detection. The fundamental disadvantage of this approach was the need to use concentrated HCl. The use of aggressive reagents in the flow systems leads to the reduction of the lifetime of their elements and to the increase of the operating costs. Moreover, such systems are potentially dangerous and require special care during their operation. Recently, Alonso-Mateos [14] proposed a method for sequential determination of bromate and chlorite ions by kinetic differentiation in the continuous-flow mode. Although the method was simple and sensitive, the results were strongly influenced by chemical conditions; hence, their precision was relatively poor.

Aforementioned features discourage potential users from using the suggested systems, which have little chance to be applied to the routine environmental analysis in the proposed shape. Therefore, efforts have been made to develop methods based on simple equipment available in any environmental laboratory and on analyst-friendly analytical procedures.

This paper presents an alternative analytical method for routine determination of chlorite ions in drinking water. Chlorite ions were determined indirectly using the flow technique in combination with spectrophotometric detection. Analytical signal was measured for the coloured complex of Fe^{2+} with *o*-phenanthroline.

EXPERIMENTAL

Reagents

A 1000 mg L⁻¹ stock standard solution of NaClO₂ was prepared by dissolving 80% NaClO₂ (Merck, Germany) in water acidified to pH 5. The solution was stored at 4°C for 2 weeks. Synthetic samples and standard solutions of chlorites were prepared freshly by appropriate dilution of the stock standard solution with water acidified to pH 5.

A 40 mg L⁻¹ Fe(II) solution was prepared by dissolving of a weighed amount of FeCl₂·4H₂O (Sigma-Aldrich, Germany) in water acidified to pH 5. 1% (v/v) HCl was prepared by diluting 32% (*ca* 10 mol L⁻¹) HCl (Merck, Germany). 0.25% solution of *o*-phenanthroline was prepared by dissolving a weighed amount

of o-phenanthroline monohydrate G.R. $C_{12}H_8N_2 \cdot H_2O$ (Lach-Ner, Czech Republic) in 1% (v/v) HCl. 5% solution of trisodium citrate and 0.2 mol L^{-1} solution of ammonium chloride were prepared by dissolving the weighed amounts of $C_6H_5Na_3O_7 \cdot 2H_2O$ (POCh, Gliwice, Poland) and NH_4Cl (POCh, Poland) in water. 0.1 mol L^{-1} carbonate-free NaOH solution was prepared by appropriate dilution of the weighed amount of NaOH Titrisol standard solution (Chemed, Poland).

For interference studies, solutions of cations in the form of chloride salts and solutions of anions in the form of potassium or sodium salts were used. These solutions were prepared by dilution of the appropriate stock standard solutions prepared using Titrisol standards (Merck, Germany) with water or 1% (v/v) HCl solution.

Analytical reagent grade chemicals and water from reverse osmosis were used throughout.

Instrumentation

The proposed manifold is presented in Figure 1. It consisted of an Ismatec peristaltic pump (Ismatec S.A., Switzerland), a LZ-1020 eight-channel two-position directive valve (Zhaofa, China), a set of PTFE transporting tubings, mixing coils and elastic Tygon tubes with various diameters. The flow system was coupled to a Lambda UV-VIS spectrophotometer (Perkin Elmer, USA) with 0.018 mL-in-volume flow cells of optical path length of 10 mm (Hellma GmbH, Germany). Measurements were performed at the wavelength $\lambda = 512$ nm.

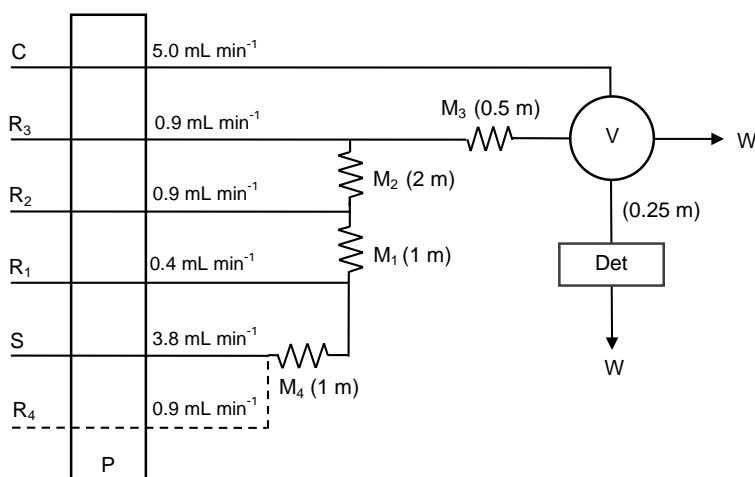


Figure 1. Flow manifold for determination of ClO_2^- ions; S – sample or standard solution, R_1 – Fe(II), R_2 – o-phenanthroline, R_3 – sodium citrate, R_4 – reagent tested as an interferent, C – carrier, P – peristaltic pump, M_1 – M_4 – mixing coils, V – directive valve, Det – detector (UV-VIS spectrophotometer, $\lambda = 512$ nm), W – waste

Ion chromatography method was applied to the determination of chlorites [8]. A DX 600 chromatograph (Dionex Corporation, USA) equipped with an AS9-HC 4×25 mm column, an Ion Pac AG9-HC preliminary column, a LC 30 stove, a ED 50 conductivity cell, a DP 50 gradient pump, and a loop of 0.360 mL capacity were used. Validation parameters of the method (obtained from the Municipal Water & Sewage Company, Cracow, Poland) were: RSD = 9.14% ($n = 2$), LOD = 0.002 $mg L^{-1}$, LOQ = 0.007 $mg L^{-1}$.

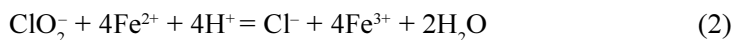
Natural samples

Water samples were taken directly from taps. Water was supplied by three Drinking Water Treatment Plants in Krakow and originated from one of the rivers: Raba, Rudawa, and Dłubnia. Each sample was filtered through a 0.45 μm pore diameter membrane filter and stabilized using 0.1 mol L⁻¹ NaOH, which was added to the sample to achieve pH = 10. Directly prior to the measurement the sample was degassed with nitrogen for 15 min and acidified with 1% (v/v) HCl to pH = 5.

RESULTS AND DISCUSSION

Method

The proposed method was based on the oxidation of Fe²⁺ ions to Fe³⁺ ions using chlorite ions in an acidic medium. The reaction proceeded according to the equation below:



Analytical signal was measured for the coloured complex of Fe(II) ions with o-phenanthroline stabilized in the sodium citrate stream.

Standard solutions of chlorites of concentrations ranging from 0.1 to 0.8 mg L⁻¹ were used for calibration purposes. Concentration of Fe(II) solution was fixed at 8 mg L⁻¹, which was excessive with respect to that of chlorites, according to the stoichiometry of reaction (2). The calibration function was decreasing as the amount of Fe(II) decreased proportionally to the increase of the analyte concentration. Each sample and standard solution was analysed five times under the same optimized conditions.

Optimization studies

In the flow system designed for the proposed method (Fig. 1) the sample solution was successively merged and mixed with streams of Fe(II), o-phenanthroline and sodium citrate. Afterwards, it was injected to the carrier stream (water) and delivered with this stream to the spectrophotometer. To examine the interference effects, an additional tube was installed to the system (R_4); it allowed the interferent solution to be merged with the sample prior to other reagents.

Figure 2 shows the changes of the measured analytical signal in relation to the sample pH. Stable absorbance values were observed in the range of low pH. For pH > 6 the signal suddenly declined indicating nearly complete oxidation of Fe²⁺ to Fe³⁺. In the subsequent analyses pH of the samples was set at 5.

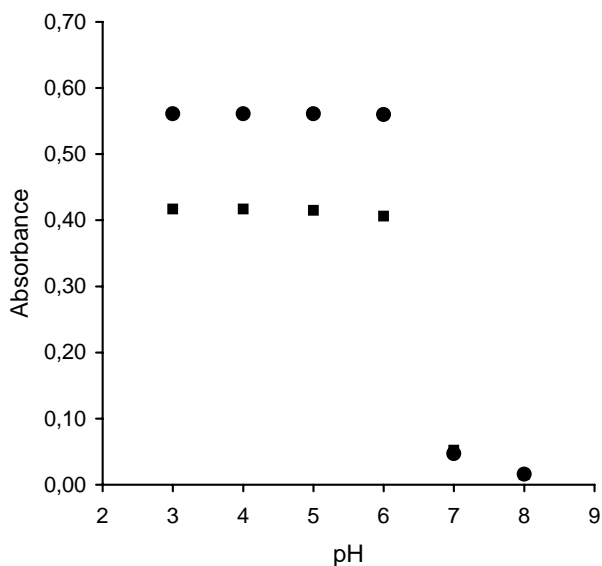


Figure 2. The influence of pH of sample solutions on the analytical signal; concentration of ClO_2^- – 0.0 (●) and 0.8 (■) mg L^{-1}

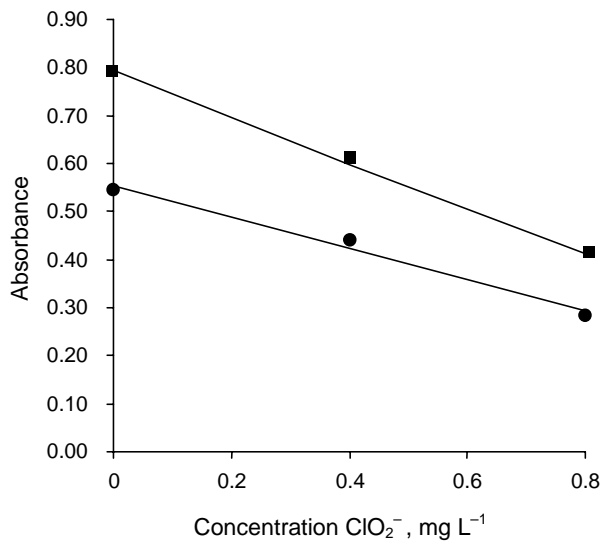


Figure 3. The influence of o-phenanthroline (0.25%) and citrate (5%) solutions on the sensitivity of the method, when either citrate (●) or o-phenanthroline (■) solution was added as first

It was also evidenced that concentrations of o-phenanthroline and sodium citrate solutions were of little importance for the sensitivity of the method. Thus, both rea-

gents were used in the concentrations of 0.25% and 5%, respectively; these values were sufficient to initialize a coloring reaction with Fe(II). Moreover, it was observed that the addition order of these reagents played an important role (o-phenanthroline should be added first; Fig. 3).

The lengths of the mixing coils M_1 , M_2 , M_3 and M_4 (Fig. 1) were insignificant for both the sensitivity and precision of the method, provided that they were not shorter than 1.0, 2.0, 0.5 and 1.0 m, respectively. As the sensitivity increased linearly with the increase of the sample flow rate, the sample was delivered at relatively high flow rate (3.8 mL min^{-1}). In order to ensure possibly the lowest sample dilution, the reagents (Fe(II), o-phenanthroline and sodium citrate) were propelled at much lower rates (0.4 , 0.9 and 0.9 mL min^{-1} , respectively) but their concentrations were sufficiently excessive (8 mg L^{-1} , 0.25% and 5%, respectively). The final fixed values of all instrumental parameters are shown in Figure 1.

Furthermore, it was observed that the concentration of chlorites in water samples taken from a rarely used tap was very low (Fig. 4) as chlorites were decomposed naturally. Based on the experimental results, the optimum sampling time was set at 10 min after the tap had been turned on.

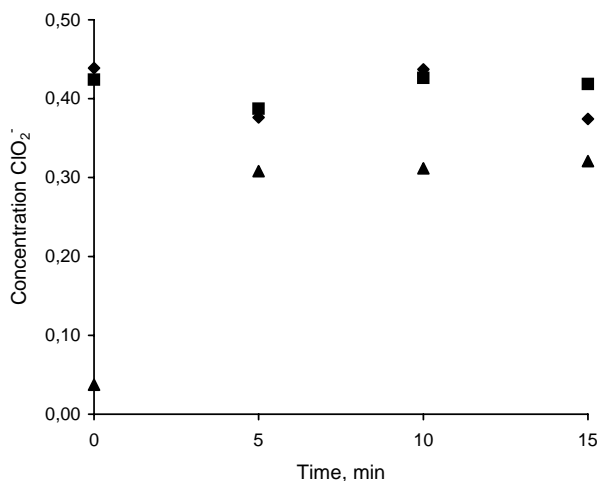


Figure 4. Time changes in the concentration of ClO_2^- ions found in three different samples (▲, ■, ◆); time was measured from the moment of turning on a tap to the beginning of sample collection; (▲) – the case of the infrequently used tap

Validation studies

Linearity of the method was examined in the concentration range of chlorites 0.10 – 8.0 mg L^{-1} . Calibration graph was found to be linear within the range

0.10–6.0 mg L⁻¹. Based on the linearity test [15], the limit of detection (LOD) and the limit of quantification (LOQ) were estimated as 0.01 and 0.03 mg L⁻¹, respectively. Precision of the method (measured as the repeatability of 5 analytical results obtained for each of 5 different water samples) was found to be 0.40% (RSD).

Recovery of the analyte (RV) was determined in the analysis of tap water samples. Each sample was analyzed three times without addition of chlorite ions and in the presence of chlorites added in the amounts of 0.2, 0.4 and 0.6 mg L⁻¹. The obtained results are presented in Table 1. They show high accuracy of the determinations. The results for the Dłubnia river water samples were slightly worse than those obtained for the water samples from two other intakes. The probable reason for this difference was that the water in the Dłubnia River has a relatively richer biological matrix.

Table 1. Accuracy of results

River	Sample	Analyte concentration, mg L ⁻¹		RV, %
		expected value	found value	
Raba	I	0.20	0.20 (0.10)*	100.0
	II	0.60	0.61 (0.17)	101.7
	III	0.80	0.78 (0.26)	97.5
Rudawa	I	0.20	0.20 (0.25)	100.0
	II	0.60	0.62 (0.26)	103.3
	III	0.80	0.79 (0.23)	98.8
Dłubnia	I	0.20	0.23 (0.13)	115.0
	II	0.40	0.47 (0.26)	117.5
	III	0.60	0.68 (0.00)	113.3

* In parentheses the values of RSD (%) are given (n = 5).

Interference studies

The influence of different anions and cations on the analytical signal was investigated. For this purpose, synthetic solutions were prepared. They contained the analyte and an additional component present at the known concentrations. Potential interferents were taken into account and examined within the concentration ranges, at which they

occur in water classified into four different quality classes [16]. The interference effect (E_f) was calculated using the following formula: $E_f = (A_{int} - A)/A \cdot 100\%$, where A_{int} and A are the magnitudes of the signals measured for the sample solution with and without an interferent, respectively.

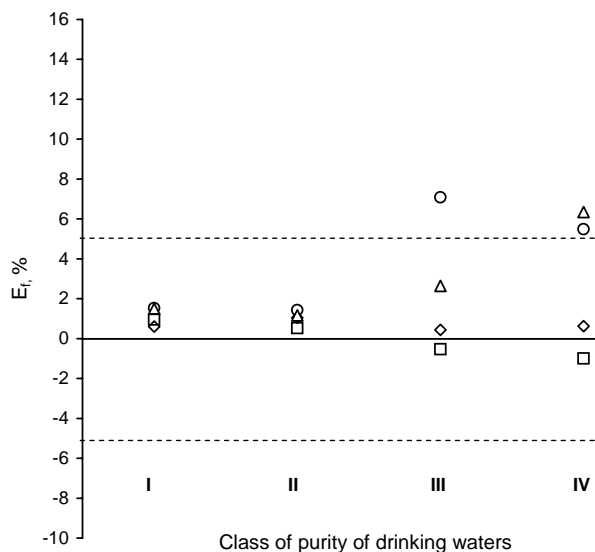


Figure 5. Interference effects caused by cations present at the concentrations corresponding to those occurring in four purity classes (I, II, III, IV) of drinking waters: \diamond Zn^{2+} (0.3, 0.5, 1.0, 2.0 $mg\ L^{-1}$), \triangle Ca^{2+} (50, 100, 250, 300 $mg\ L^{-1}$), \circ Mg^{2+} (25, 50, 100, 200 $mg\ L^{-1}$), \square Pb^{2+} (0.01, 0.01, 0.02, 0.05 $mg\ L^{-1}$); concentration of ClO_2^- – 1.0 $mg\ L^{-1}$

Figure 5 shows a number of selected examples illustrating the effect caused by the following cations: Zn^{2+} , Ca^{2+} , Mg^{2+} , Pb^{2+} . Higher positive values of E_f (above 5%) refer to water classes III and IV; such an effect was caused by the presence of Mg^{2+} and Ca^{2+} ions. Therefore, in case of drinking water with the increased content of these hardness indicators, concentration of chlorites in the samples can be underestimated. Minor effects (maximally up to + 4.5%) were observed for Cu^{2+} and Al^{3+} ions. For Na^+ and K^+ ions no changes in the analytical signal was observed.

Strong additive interference effect caused by Fe^{2+} ions could be expected. However, concentration of these ions in drinking waters is usually very low. If one suspects that larger amount of Fe^{2+} occurs in the sample, it is necessary to determine its concentration beforehand.

As presented in Figure 6, some anions had a considerable influence on the determination results of chlorite ions. For example, NO_2^- ions had such a significant impact in case of water quality class II; their effect reached 14% for water quality class IV. In the routine analyses, this phenomenon can be of importance during the spring melt

when the rivers receive waters from the fields; these waters are rich in the components washed out from the soil. Consequently, the concentration of nitrite ions in river waters increases. In case of Cl^- and ClO_3^- ions, the interference effect was not observed.

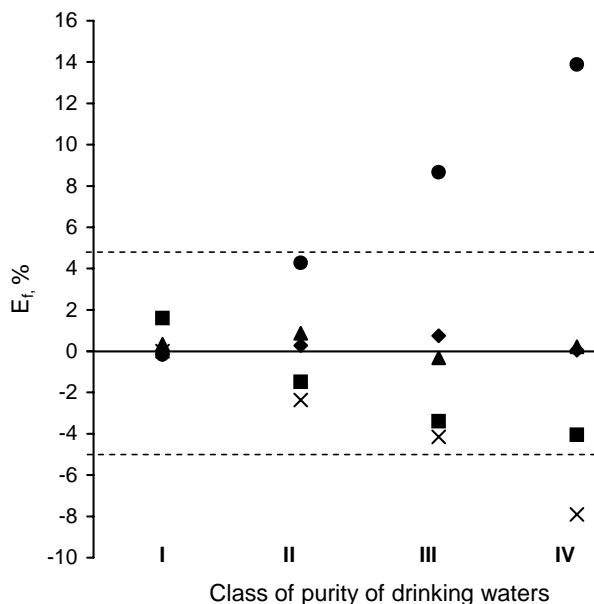


Figure 6. Interference effects caused by anions present at the concentrations corresponding to those occurring in four purity classes (I, II, III, IV) of drinking waters: ♦ NO_3^- (5, 15, 25, 50 mg L^{-1}), ● NO_2^- (0.03, 0.1, 0.5, 1.0 mg L^{-1}), ■ SO_4^{2-} (100, 150, 250, 300 mg L^{-1}), ▲ F^- (0.5, 1.0, 1.5, 1.7 mg L^{-1}), × PO_4^{3-} (0.2, 0.4, 0.7, 1.0 mg L^{-1}); concentration of ClO_2^- – 1.0 mg L^{-1}

A strong multiplicative interference effect was identified in the presence of NH_4^+ ions in the solution. The analyses were carried out for different concentrations of ClO_2^- (0.2–1.0 mg L^{-1}) and NH_4^+ ions (0.90–7.22 mg L^{-1}). As shown in Figure 7, the presence of NH_4^+ ions even at a relatively low concentration (0.90 mg L^{-1}) led to a decrease in sensitivity by as much as 30%. This phenomenon was most probably caused by a decreased amount of the ions accessing the reagent, caused by decomposition due to ammonium ions. Considering the presence of trace amounts of NH_4^+ ions in natural samples, this effect should be insignificant in practice (the largest allowable amount of NH_4^+ ions is 5.4×10^{-4} mg L^{-1} [17]). However, attention should be paid to the fact that for the purposes of this method Fe(II) must be prepared in the form of a chloride instead of the customary used Mohr's salt.

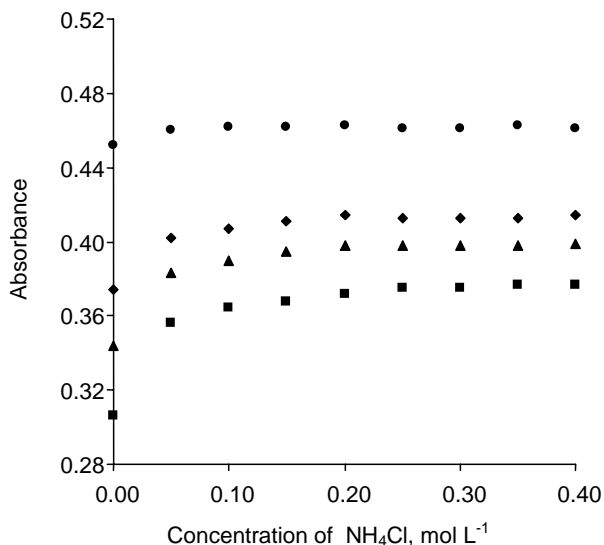


Figure 7. Influence of NH₄⁺ on the analytical signal of ClO₂⁻; ClO₂⁻ concentrations: 0.2 (●), 0.6 (◆), 0.8 (▲) and 1.0 (■) mg L⁻¹

Analysis of natural samples

The research involved analyses of drinking tap water samples. The water originated from the rivers: Raba, Rudawa and Dłubnia. The results were compared to those obtained for the same samples analysed by ion chromatography, the method used in routine water analysis. Each sample was analyzed five times using the spectrophotometric method and once using the chromatographic method. Table 2 shows the obtained results (mean values in case of the proposed method).

Table 2. Comparison of the results of chlorite ions determination obtained by spectrophotometric and chromatographic methods

River	Sample	Analyte concentration found, mg L ⁻¹	
		Spectrophotometry*	Ion chromatography
Raba	I	< LOQ	< LOQ
	II	0.02 (0.08)	0.01
	III	0.03 (0.12)	0.02

(Continuation on the next page)

Table 2. (Continuation)

River	Sample	Analyte concentration found, mg L ⁻¹	
		Spectrophotometry*	Ion chromatography
Rudawa	I	< LOQ	< LOQ
	II	0.04 (0.00)	0.03
	III	0.38 (0.15)	0.48
Dłubnia	I	0.35 (0.32)	0.38
	II	0.48 (0.17)	0.44
	III	0.39 (0.18)	0.28

* In parentheses the values of RSD (%) are given (n = 5).

The results obtained by the proposed method were in most cases very similar to those obtained by the ion chromatography method. Larger differences were observed only for some samples containing chlorites at high concentrations (> 0.2 mg L⁻¹). Considering the results of earlier recovery analyses (Tab. 1) the following was concluded. Despite the probability of considerable errors in determination of chlorite ions in the samples with complex matrices, the proposed method offers reliable results. Moreover, as evidenced, the results of the analysis of the same samples obtained applying both methods were within the allowable limits [1, 17] suggested by the directives of EPA for chlorite ions analysis [18].

CONCLUSIONS

Flow method with spectrophotometric detection for indirect determination of chlorite ions *via* determination of Fe(II) complex with *o*-phenanthroline was developed. The study confirmed the usefulness of the proposed method for determination of chlorite in drinking water within the applicable concentration ranges of these ions [2, 18] as well as exemplified the use of the flow method to improve the routine analyses. The proposed procedure was fast and inexpensive. The results were obtained with good accuracy and good precision, while the time for a single measurement was approximately 35 s.

Due to its advantages, the method can be considered as an alternative approach to the ion chromatography method towards determination of chlorite ions in drinking

water. Its weakness is an additive influence of Fe^{2+} ions on the analytical signal. For this reason, the method can be applied only when the concentration of these ions is very low. Otherwise, it is necessary either to remove them from a sample or to determine accurately their concentration beforehand.

The results obtained by the developed method can be overestimated due to the changes of pH of the analyzed sample during the analysis or the presence of a complex matrix, which may have an unpredictable effect on the determination results. However, this problem concerns mainly the waters from quality class IV, which are rarely used for consumption, mostly due to the necessity to apply additional treatment procedures, which imply a considerable rise in costs.

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REFERENCES

1. Drinking Water Directive 98/83/EC (1998).
2. WHO, Guidelines for Drinking-Water Quality, 3rd edn, Recommendations, Geneva (2004).
3. Nawrocki J., Biłozora S., *Uzdatnianie wody. Procesy chemiczne i biologiczne*, PWN, Warszawa–Poznań 2000.
4. Masschelein W.J., *Unit processes in drinking water treatment*, Marcel Dekker Inc. New York–Basel–Hong Kong 1992.
5. Dietrich A., Ledder T.D., Gallagher D.L., Grabeel M.N. and Hoehn R.C., *Anal. Chem.*, **64**, 496 (1992).
6. Shminke G. and Seubert A., *J. Chromatogr. A*, **890**, 295 (2000).
7. Bnghui Z., Zhixiong Z. and Jing Y., *J. Chromatog. A*, **1118**, 106 (2006).
8. International Standard ISO 10304–4 (1997).
9. Praus P., *Talanta*, **62**, 977 (2004).
10. Philippi M., Santos H.S., Martins A.O., Azevedo C.M.N. and Pires M., *Anal. Chim. Acta*, **585**, 361 (2007).
11. Pepich B.V., Dattilio T.A., Fair P.S., Munch D.J., Gordon G. and Körtvélyesi Z., *Anal. Chim. Acta*, **596**, 37 (2007).
12. Ohura H., Imato T. and Yamasaki S., *Talanta*, **49**, 1003 (1999).
13. Miller K.G., Pacey G.E. and Gordon G., *Anal. Chem.*, **57**, 7347 (1985).
14. Alonso-Mateos A., Almendral-Parra M.J. and Fuentes-Prieto M.S., *Talanta*, **76**, 8928 (2008).
15. International Standard ISO 8466–1 (E) (1990).
16. Minister of the Environment Protection Directive Dz. U. 32.284, 1st March (2004).
17. Minister of Health. Directive Dz. U. 61.417, 6th April (2007).
18. Federal Register 68, 159, 18th August (2003), Proposed Rules.

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