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DETERMINATION OF CHLORITE IN DRINKING WATER AND RELATED ASPECTS OF ENVIRONMENT PROTECTION

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INTRODUCTION

Before the advent of the 20th century contaminated water was the main reason for dissemination of cholera, typhoid fever and other lethal deceases. The use of treated water has reduced the death rate among those human populations who receive such water. At present, the main sources of water contamination are chemicals, industrial waste, airborne dust and gases as well as municipal waste rather than bacteria and viruses. Monitoring water quality is much easier in the countryside than in towns, where people have no choice but must use tap drinking water and believe that its quality is permanently controlled by municipal services responsible for water quality.

Those in charge of water treatment plants are responsible for water disinfection and for maintaining microbiological purity of water. Disinfection is to destroy or postpone multiplication of pathogenic organisms (Nawrocki, Biłozora 2000).

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Despite constant improvements in water treatment technology, drinking water may contain harmful products created during water treatment processes.

There are several chemicals used in water treatment processes, including chlorine, ozone, chlorine dioxide, chloramines and iodine. Nowadays, the use chlorine compounds is not recommended as they react with organic compounds creating harmful chemical products and adversely affecting organoleptic properties of water. Ozone reacts more rapidly with waterborne impurities but quickly disintegrates in water and thus it cannot maintain good water quality for a long time. Chlorine dioxide appears to be the best disinfecting agent because is more stable than ozone and less harmful than chlorine. Advantages of chlorine dioxide are as follows: high effectiveness and good oxidizing properties, good antiviral and antibacterial properties, good phenol oxidizing capability (contrary to chlorine which produces chlorophenoles and unpleasant odour), consequently, it brings about considerable improvement of water quality in terms of its organoleptic properties (KOWAL, ŚWIDERSKA-BRÓZ 1996, KOWAL 1997, WATANABE et al. 1997, NAWROCKI, BIŁOZORA 2000, KATZ, NARKIS 2001).

Among the byproducts of a disinfection process with chlorine, dioxide chlorite ions are especially harmful for health. They appear in the following reaction:

$$2ClO_2 + H_2O = HClO_2 + HClO_3$$

It is believed that concentration of chlorite ions corresponds to 80% of chlorine dioxide maximum (MOSSAKOWSKA 1999). It has been proved that these ions can be to blamed for hemolytic anemia, which is caused by oxidation of cell membranes of erythrocytes (MAĆKIEWICZ et al. 2003). Moreover, it has been confirmed that chlorite ions present in drinking water in concentrations higher than 1.2 $mg \cdot dm^{-3}$ are believed to be harmful; when exceeding 1000–1500 $mg \cdot dm^{-3}$ they produce acute effects (KOWAL 1997, KATZ, NARKIS 2001).

In the light of the above considerations, reliable control of chlorite ions concentration in drinking water is an important problem. According to the national regulations (Ministry of Health and Social Care 2002), the allowable concentration of chlorite ions is 0.200 $mg \cdot dm^{-3}$ and the method of ion chromatography is the only recommended analytical method for determination of these ions (Polish Norms 2002). Unfortunately, ion chromatography is relatively expensive in respect of both instrumental and exploitation costs, hence it is not available at every analytical laboratory. This has encouraged us to try and develop at our laboratory an alternative method for routine determination of chlorite ions in water.

MATERIAL AND METHODS

Sandard solutions and synthetic water samples were prepared by dilution of stock solution containing ClO_2^- at a concentration 1000 $mg \cdot dm^{-3}$ with the use of water from reverse osmosis. Samples of drinking water were taken from water-supply systems delivering water for citizens of Krakow from the Rudawa, Dłubnia and Raba rivers. Water was allowed to flow freely for 15 minutes before a sample was collected into a polyethylene or glass 1 liter bottle. All samples were filtered using the membrane filter with 0.450 µm pore decimeter. The pH value was maintained at 10 using 1 cm^3 of NaOH per 100 cm^3 of the sample volume. The concentration of NaOH solution was equal to 0.1 $mol \cdot dm^{-3}$. Just before each measurement a sample was de-oxidized for 15 using nitrogen and finally the pH was adjusted to 5.5 using 1% (v/v) HCl.

Samples were analysed by indirect method using dedicated flow system and a spectrophotometer UV/VIS SPEKOL 11 (C. Zeiss, Germany). The flow system, schematically presented in Figure 1, was used for mixing the chlorite solution (sample or standard solution) with $[(NH_4)_2SO_4][FeSO_4][H_2O]_6$ solution containing 8 $mg \cdot dm^{-3}$ Fe^{2+} (pH = 5) in order to initiate the following reaction:

$$ClO_2^- + 4Fe^{2+} + 4H^+ = Cl^- + 4Fe^{3+} + 2H_2O$$

The solution thus obtained was mixed with 0.25% (v/v) solution of 1,10-phenanthroline in order to obtain a coloured ferrous complex (II), which was next stabilized in a stream of 5% (v/v) sodium citrate. Measurements were taken at the wavelength λ=512 nm. Standard solutions with ClO_2^- of concentration from 0.01 to 1.00 $mg \cdot dm^{-3}$ were used for calibration.

Results of the determination of chlorite ions obtained by our method were compared with the results obtained by the ion exchange chromatography method in the environmental laboratory of the Municipal Water&Sewage Company, Kraków. A DX 600 chromatograph was used (Dionex Corporation, USA) equipped with the following subassemblies: AS9 – HC 4x25 mm column, preliminary co-

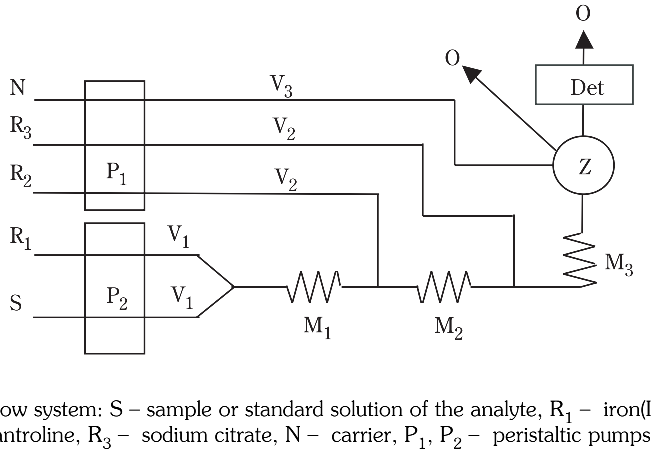

Fig. 1. The flow system: S – sample or standard solution of the analyte, R_1 – iron(II) solution, R_2 – 1,10-phenantroline, R_3 – sodium citrate, N – carrier, P_1, P_2 – peristaltic pumps propelling the solutions, V_1, V_2, V_3 – tubes transporting the solutions with flow rates 1,95; 0,90; 7,90 $ml \cdot min^-1$, respectively, M_1, M_2, M_3 – mixing coils of 100, 200, 44 cm in length, respectively, Z – valve, Det – detector (spectrophotometer UV/VIS, λ=512 nm), O – waste

lumn Ion Pac AG9-HC, LC 30 stove, conductivity cell ED 50, progressive pomp DP 50 and the loop way of 0.360 cm^3 capacity.

RESULTS AND DISCUSSION

The preliminary investigations included the optimization of chemical and instrumental conditions as well as the evaluation of analytical parameters of the spectrophotometric method developed. The method was next used for analysis of natural samples of drinking water collected on various days. Then the same samples were analyzed using the ion exchange chromatography. The results are shown in Table 1.

When the spectrophotometric method was used, each sample was analyzed three times under identical conditions. Precision of the results was found to be below 0.300 % (RSD). This is a proof that the method makes it possible to determine chlorite ions with very small random error.

Accuracy of the proposed method was evaluated by comparison of the results obtained for samples with and without the analyte (i.e. by using the recovery test). The data shown in Table 1 indicate that the accuracy of results obtained for

Table 1

Results of the determination of chlorite(III) ions in drinking water samples obtained by spectrophotometric and ion chromatography methods

River	Sample	True value (mg dm^{-3})	Spectrophotometric method		Ion chromatography method	
			found value (mg·dm^{-3})	RE (%)	found value (mg·dm^{-3})	RE (%)
Raba	I	? 0.200*	0.010 0.184	- 8.000	0.000 -	- -
	II	? 0.200*	0.021 0.198	- 1.000	0.000 0.220	10.00
	III	?	0.020	-	0.000	-
Rudawa	I	?	0.009	-	0.000	-
	II	? 0.200*	0.015 0.181	- 9.591	0.000 0.230	- 15.00
	III	?	0.036	-	0.000	-
Dłubnia	I	?	0.353	-	0.190	
	II	? 0.200*	0.498 0.146	- 27.00	0.220 0.170	- 15.00
	III	?	0.387	-	0.112	-

* the concentration of the analyte added to a sample

the samples of relatively low natural concentration of chlorite ions (i.e taken from the Raba and Rudawa) was satisfactory and usually better than of that obtained by ion exchange chromatography. The biggest error was recorded for the sample from the Dłubnia (sample II), which contained the highest amount of chlorite. It is worth noticing that laboratory regulations allow for 25% accuracy of chlorite determination (report on validation methods) and this means that nearly all the data obtained by both analytical methods are sufficiently reliable.

The results proved that chlorite concentration obtained for almost all samples assayed did not exceed (or slightly exceeded) the acceptable level (0.200 mg·dm^{-3}). The only exception was a sample with the analyte concentration determined in the sample II from the Dłubnia river, which was two-fold higher than the allowable value.

As shown in Table 1, concentrations of chlorite ions varied for each water sample depending on time of the day. Certainly, these values are mainly affected by amount of chlorine dioxide used on a given day for disinfection purposes. Furthermore, it should be remembered that the chemical composition of drinking water depends on water supply, which may be reduced under unfavorable weather conditions and sometimes must be supplemented from other sources, where chlorite concentration and treatment procedure are different.

CONCLUSIONS

As revealed, the spectrophotometric method developed allows chlorite ions to be determined in drinking water with very good precision and satisfactory accuracy. When using the flow technique, the entire analytical procedure can be automated, which makes analyses easier and faster. In addition, it enables maintaining constant chemical and instrumental conditions of determinations, which means good repeatability of analytic results, the fact that has been confirmed experimentally. Moreover, a set of instruments for flow analysis connected to a spectrophotometer UV/VIS, unlike instruments necessary for ion exchange chromatography, can take the form of a small analytical system, easy to install and service in field conditions, but clever enough to monitor the content of chlorite in water at optionally selected measurement points.

The method of chlorite determination in drinking water presented in this paper is very competitive to the ion-chromatography method for the following reasons:

– chromatography can be effectively used if it is capable to separate different components of the sample analyzed and to determine these components under identical chemical and instrumental conditions. The use of ion exchange chromatography for the determination of chlorite requires a special preliminary step for the sample preparation (Polish Norms 2002) which creates unfavorable analytic conditions for determination of other analytes (except chlorate), which are important for environmental protection. Thus, the method becomes uneconomical and the cost of individual analyses is comparatively high.

– Duration of chlorite determination in water sample using the spectrophotometric method is much shorter than that required for the ion exchange chromatography method (approximate test times are equal to 1 and 30 min, respectively). In addition, the high rate of spectrophotometric method allows for frequent recalibration, which improves accuracy of analytical results.

– In ion-chromatographic determination of chlorite ions peaks corresponding to the analyte and to organic compounds frequently partly overlap. This additive interference effect is a potential source of systematic errors of analytical results. It may have been the reason for the difference between the results of chlorite determination obtained by the two methods for sample II taken from the Dłubnia river. The spectrophotometric method proposed is free from this kind of interference.

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Key words: chlorite, UV/VIS spectrophotometry, drinking water, flow analysis.

Abstract

One possible method of drinking water treatment is chlorine dioxide disinfection. This technology, however, requires reliable control of its byproducts, including chlorite ions., which pose a threat to human health. In this paper an original procedure for flow indirect determination of chlorite in drinking water was described. This method relies on oxidization of chlorite ions by iron(III) in acid environment measurement of the spectrophotometric signal for the phenanthroline/iron(II) complex. The determinations were carried out by flow analysis with the use of a dedicated set of flow instruments. The method was used for analysis of natural samples collected from various water intakes in Kraków. The new analytic approach was compared with the routinely applied ion chromatography method.

OZNACZANIE CHLORANÓW W WODACH WODOCIĄGOWYCH W ASPEKCIE OCHRONY ŚRODOWISKA

Słowa kluczowe: chlorany(III), spektrofotometria UV/VIS, woda wodociągowa, analiza przepływowa.

Abstrakt

Jednym ze sposobów uzdatniania wody pitnej jest jej dezynfekcja tlenkiem chloru(IV). Ważnym zadaniem, jakie wiąże się jednak z tym procesem, jest wiarygodna kontrola zawartości produktów ubocznych w postaci jonów chloranowych(III), stanowiących duże zagrożenie dla zdrowia człowieka. W pracy opisano oryginalną procedurę pośredniego oznaczania chloranów(III) w wodach. Polega ona na wykorzystaniu reakcji chloranów(III) z jonami żelaza(II) w środowisku lekko kwaśnym i pomiarze spektrofotometrycznego sygnału dla jonów żelaza(II) w obecności 1,10-fenantroliny. Oznaczenia wykonywano techniką przepływową z użyciem dedykowanego zestawu instrumentalnego. Metodę zastosowano do analizy próbek pobranych z różnych ujęć wody pitnej w Krakowie. Dokonano porównania opracowanego podejścia analitycznego z rutynowo stosowaną metodą chromatografii jonowej.