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Determination of fluoride anions in drinking water samples using of ion chromatography technique

Oznaczanie jonów fluorkowych w próbkach wód pitnych metodą chromatografii jonowej

INTRODUCTION

Fluorides are an important anions present in various environmental, chemical and food samples. They are an essential oligo-element, beneficial for growth and development of bones and teeth [3,5]. This element plays a central role in the prevention of dental caries however, it is toxic at high concentrations [2]. The recommended for dental health optimal fluoride intake level ranges from 0.05 to 0.07 mg/kg/day [8,1]. Too large quantities of fluorides are the primary reason for the prevalence of dental and skeletal fluorosis and also show renal, gastrointestinal and immunological toxicity.

In view of these facts it is necessary to monitor the content of this anion in human diet. One of the sources of fluoride is drinking water.

The objective of this study was to investigate the fluorides (F^-) content of various commercially available drinking waters.

MATERIALS AND METHODS

Chemicals and standard solutions. All reagents: $NaHCO_3$, Na_2CO_3, $AgNO_3$, and standard of fluoride were of analytical grade from Merck (Germany). Water was redistilled and deionised by use of EasyPure RF system (Bearnsted, USA). The efficiency of this process was checked conductometrically, the resistance of water was 18 MΩ-cm. The analyzed samples of water were purchased at a local market. The standard solutions in the concentration range from 0.001 to 5ppm were prepared by dilution of stock solution (1000ppm). Sample preparation. The samples of commercially available waters were previously degassed by using ultrasonic bath and purified by SPE technique on a sorbent based on silica gel modified with polyaniline to remove bromide and chloride ions.

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H P L C c o n d i t i o n. The samples were analyzed using an ion chromatograph DX-500 IC (Dionex USA) with a conductometric detector and suppression of the eluent background in the recirculation mode system. Producer`s precolumn AG14A and AS14A column, suppressor column ASRS and sample 25µL loop were used. As eluent, aqueous solution containing 3.5 mM (0.37 g) of Na_2CO_3 and 1 mM (0.084 g) of $NaHCO_3$ were used. The flow rate was 0.3mL/min, temperature 30°C.

RESULTS AND DISCUSSION

Fluorides are an important component of diet from the viewpoint of human health. The drinking water is valuable source of these ions but their content should be monitored because they are toxic in large amounts. According to WHO the maximum permissible limit of fluoride in drinking water is 1.5 mg L^{-1}, while in China it is only 1.0 mg L^{-1}. Polish regulations are consistent with the recommendations of WHO [6]

In the presented paper, the concentration of fluorides in fifteen popular commercially available drinking waters was investigated. The waters with different content of mineral components from different parts of Poland were tested by ion chromatography (IC).

The appropriate correlation equation to quantification was selected on the basis of the F statistic values expressed in formula [7]:

$$F = \frac{R^2}{1-R^2} \cdot \frac{n-k}{k-1}$$

where:

R- correlation of determination

n - number of measurements

k - number of explanatory parameters

The F values for different types of regression equations (Table 1) indicate that linear regression is optimal for fluoride. The linear regression data and validation parameters such as relative standard deviation, confidence interval, LOD and LOQ are summarized in Table 2. The obtained calibration curve for determination of fluoride ions is presented in Fig. 1.

Table 1. The values of F statistics of different correlation equations for fluoride

y=a+bx	242
y=a+bx+cx2	135
y=bx	109
y=bx+cx2	176

Table 2. Linear regression data and validation parameters to quantification of fluoride

Parameter	W*	Standard deviation s	t=W/s t	95% confidence interval (level)		P>t	LOD	LOQ
		y= a +bx		R^2 = 0,9973		F =6616		
a	-0.000158	0.000059	-2.70	-0.000281	-0.000035	0.0148	0.003	0.009
b	0.02581	0.00032	81.34	0.02515	0.02648	0		

*- $W_i = \frac{n \cdot s_i^{-2}}{\sum_{i=1}^{n} s_i^{-2}}$

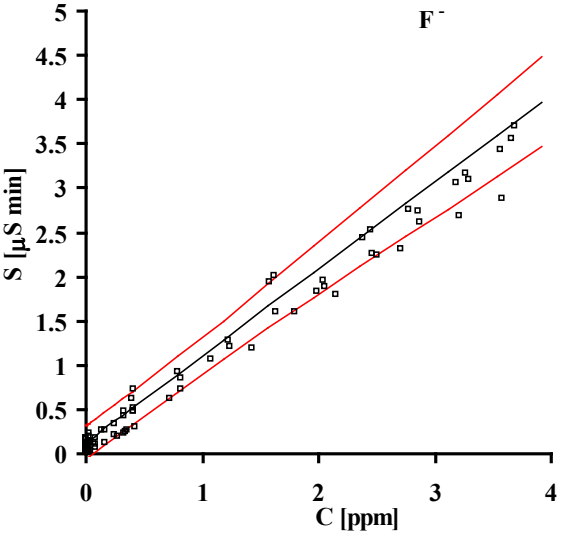

Figure 1. Calibration curve for fluoride ions

The high concentration of the other ions especially chloride (matrix effect) in water samples is an important analytical problem. SPE technique was successfully used to remove the undesirable matrix effect (Fig. 2).

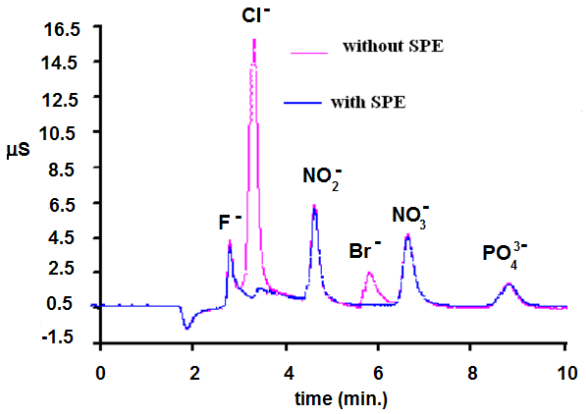

Figure 2. The example of chromatogram of investigated water before and after SPE purification

The amounts of fluoride anion in all investigated samples of commercially available drinking water ranged from 0.11 to 0.41 ppm (Table 3). These values are within the Polish standards. The concentrations of determined ions were below the declared values.

Table 3. The concentrations of fluoride (ppm) in analyzed drinking water.

Sample of the water	The concentrations of fluoride (ppm) n = 5		
	Declared	Determined ± SD (n=5)	% of difference
„Nałęczowianka" carbonated	0.24	0.20 ± 0.016	20.00
„Nałęczowianka" noncarbonated	0.3	0.22 ± 0.013	36.36
„Cisowianka" carbonated	-	0.17 ± 0.012	-
„Cisowianka" noncarbonated	-	0.22 ± 0.015	-
„Muszynianka"	-	0.33 ± 0.013	-
„Vita" carbonated	-	0.41 ± 0.021	-
„Kropla Beskidu" noncarbonated	-	0.30 ± 0.014	-
„Mazowszanka"	0.42	0.39 ± 0.018	7.69
„Arctic" carbonated	0.17	0.11 ± 0.012	54.55
„Arctic" noncarbonated	0.17	0.12 ± 0.012	41.67
„Primavera" noncarbonated	0.08	0.10 ± 0.011	20.00
„Świtezianka"	0.20	0.18 ± 0.012	11.11
„Woda Maksymiliana"	0.30	0.24 ± 0.015	25.00
„Oaza" carbonated	0.22	0.20 ± 0.015	10.00
„Oaza" noncarbonated	0.08	0.11 ± 0.010	27.27

CONCLUSION

The amount of fluoride anions in all investigated samples of commercially available drinking water did not exceed Polish standards.

The obtained results indicate that the method of ion chromatography is a reliable technique for the determination of fluoride ions in aqueous solutions. The fluoride content can be determined on ppb level.

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ABSTRACT

The determination of fluorides in drinking water was performed using ion chromatography. The samples of commercially available waters were previously degassed and purified by SPE technique to remove bromide and chloride ions. Subsequently fluoride ions were determined on ion chromatograph DX-500 IC (Dionex USA) with a conductometric detector. As eluent, aqueous solution containing 3.5 mM (0.37 g) of Na_2CO_3 and 1 mM (0.084 g) of $NaHCO_3$ was used. Amount of fluoride anions in all investigated samples of commercial available drinking water ranged from 0.11 to 0.41 ppm. These values did not exceed Polish standards.

Keywords: fluoride, ion chromatography, analysis of drinking water, SPE.

STRESZCZENIE

Metodą chromatografii jonowej oznaczono zawartość jonów fluorkowych w komercjalnie dostępnych wodach pitnych. Analizowane próbki były odgazowywane i oczyszczane techniką SPE w celu usunięcia jonów bromkowych i chlorkowych. Następnie jony fluorkowe oznaczano za pomocą chromatografu jonowego DX-500 IC (Dionex USA) z detekcją konduktometryczną. Jako fazę ruchomą stosowano wodny roztwór zawierający 3.5 mM (0.37 g) Na_2CO_3 i 1 mM (0.084 g) $NaHCO_3$. We wszystkich analizowanych wodach zawartość fluorków była poniżej dopuszczalnej normy i mieściła się w granicach 0.11-0.41 ppm.

Słowa kluczowe: florki, chromatografia jonowa, analiza wody pitnej, SPE