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Research Article

Determination of Trace Amounts of Zirconium and Fluoride in Tap Water and Bottled Water Samples Using High Performance Liquid Chromatography

Yüksek Performanslı Sıvı Kromatografi ile Musluk Suyu ve Şişelenmiş Su Örneklerinde Zirkonyum ve Florürün Eser Miktarlarının Belirlenmesi

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Abstract

The determination of trace amounts of zirconium and fluoride in various matrixes (tap and bottled water) were investigated by high performance reversed phase liquid chromatography. High performance liquid chromatography (HPLC) was used for determination of zirconium and fluoride based on their formed complex with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP). Solid-phase extraction (SPE) along with high performance liquid chromatography was used for the analysis. Under optimum conditions, the detection limits for Zr(IV) and fluoride were 0.4 µg/L, and 0.015 µg/L, respectively. Recoveries, 99.74–104.33% for Zr(IV) and 93.33-106.67% for fluoride were obtained. Drinking water samples were taken from different provinces in Isparta and Burdur. Bottled water samples of different brands were purchased from local markets. The sensitivity, precision and accuracy of the method parameters are sufficient when compared with other methods.

Keywords: Fluoride, HPLC, PADAP, Zr

Öz

Eser miktarlardaki zirkonyum ve florürün belirlenmesi için, çeşitli matrisler (musluk ve şişelenmiş su) yüksek performanslı tersfaz sıvı kromatografi ile incelendi. Yüksek performanslı sıvı kromatografisi, zirkonyum ve fluorürün, 2- (5-brom-2-piridilazo)-5-diethylaminophenol (5-Br-PADAP) ile oluşturduğu kompleks üzerinden belirlenmesi için kullanıldı. Katı faz ekstraksiyonu (SPE), yüksek performanslı sıvı kromatografisi ile birlikte analiz için kullanıldı. Optimum koşullar altında, Zr(IV) ve florür için dedeksiyon limitleri sırasıyla 0.4 µg/L ve 0.015 µg/L olarak bulundu. Geri kazanım, Zr(IV) için % 99.74-104.33 ve florür için % 93.33-106.67 elde edildi. İçme suları, Isparta ve Burdur'un farklı noktalarından toplandı. Şişe suları farklı marketlerden temin edildi. Metodun, duyarlılık, yöntem kesinliği ve doğruluğu parametreleri diğer metodlarla karşılaştırıldığında yeterlidir.

Anahtar Kelimeler: Fluorür, HPLC, PADAP, Zr

1. Introduction

Zirconium is used as fuel rod cladding in the nuclear reactors. Also It is used as a catalyst in organic reactions, chemical plants and, in the manufacture of water repellent textiles, in metal alloys, in the production of optical glasses with high refractive index and in dye pigments and ceramics (Wang et al. 1998, Oszwadowski et al. 1998, Shariati and Yamini 2006). Zirconium is a strategic and important element. Therefore its identification and determination are very important. Zirconium is produced from two essence minerals and mineral baddeleyite. Zirconium is a natural form of zirconium oxide or zirconia (Ells et al.1998, Hedrick 2000, Abbaspour and Baramakeh 2002, Yong 2013). Zirconium is used in laboratory pots and as a refractory material in metallurgical furnaces (Loh et al. 2005). It is also used as an alloying agent in materials. Zirconium forms alloys with a variety of metals (Ti, Nb, Ni, Fe, Sn, V, and Cr). These elements are suplemental to zirconium for progressing its mechanical properties and decreasing corrosion by water at high temperatures. Zirconium is especially appropriate in water moderated reactors because of its low neutron absorptioncross section, excellent corrosion resistance

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atmoderately increased temperatures, durability, softness, and simplicity of fabrication (Bassan et al. 2010).

Fluoride is an inorganic, nonatomic anion of fluorine and the most known electronegative element. It is very reactive element. It is not found in the elemental phase in nature. It is only in solid salts form or fluoride ions in aqueous solution (Sreedevi et al. 2006). Naturally occurring fluoride in ground water has been the subject of numerous studies in a variety of geologic settings. The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization guideline for fluoride (World Health Organization1995) is 1.5 mg/L which is the same as EEC guideline (EEC 1998). U.S. EPA, also it had determined maximum concentration 4 mg/L to head of bone fluorosis (USEPA 1985). Many epidemiological works of possible adverse effects of the long-term nibble of fluoride via drinking waters. These studies openly detect that fluoride primariliy produces more important effects on skeletal tissues (bones and teeth). Nominal concentrations of fluoride provide preservation against dental caries, especially in children. Skeletal fluorosis is observed when drinking water contains 3–6 mg of fluoride per liter. Crippling skeletal fluorosis develops where drinking water contains over 10 mg of fluoride per liter (World Health Organization 1995). Long-term back log of fluoride likely also affects thyroid function (Shariati et al. 2008), neurological effects (Balabolkin et al. 1995), induce reproductive problems (Dominguez 1995) and may affect the pineal gland (Luke 1994). Fluoride's admitted genotoxic properties may be showing up in the population as an increased risk for different cancer types (Zeiger et al. 1993, Tohyama 1996).

In order to determination of zirconium spectro analytical techniques were used; molecular fluorescence spectrophotometry (Wang et al. 1998), atomic absorption spectroscopy (AAS), inductively coupled plasma–optical emission spectrometry (ICP-OES) (Shariati and Yamini 2006; Shariati et al. 2008), laser ablation inductively coupled plasma–optical emission spectrometry (LAICP-OES) (Lin and Peng 1990), X-ray fluorescence spectroscopy (Vivit and King 2007, Nakaya et al. 2011), ultraviolet–visible spectrophotometry (UV/Vis) (Filik et al. 1998, Zhang et al. 2001, Fakhari et al. 2005, Gupta et al. 2009), neutron activation (Rebagay and Ehmann 1970), polarography (Bandyopadhyay and Vijayamohanan 1998, Mao et al. 2004, Shervedani and Bagherzadeh 2009), voltammetry (Lin and Peng 1990), ion-selective electrode (Gupta et al. 2009), liquid chromatography (Alimarin et al. 1987, Tsai and Yan 1993, Purohit and Devi 1997). And determination of the fluoride levels in various samples, different techniques have been used such as potentiometry (with fluoride sensitive electrodes), liquid chromatography, ion chromatography or spectrophotometry (Lipka et al. 2000, Tokalioglu et al. 2001, Oszwadowski et al. 1998, Oszwaldowski and Jakubowska 2003, Rajković and Novaković 2007, Savik et al. 2012)

The main aim of this work is based on the complex of Zr(IV)-F^--(5-Br-PADAP) with reversed phased liquid chromatography for determination of trace amounts of zirconium and fluoride in water samples. The procedure is simple, rapid and good reproducibility, sensitivity and accuracy. The proposed method could be successfully applied tap water and bottled water.

2. Material and Methods

2.1. Reagents

All chemicals used were of analytical reagent grade. Stock Zr solution ($ZrOCl_2$ dissolved in HNO_3) (1.00 mg/L) was purchased from Fluka (Steinheim, Germany). 5-Br-PADAP was obtained from Aldrich (Darmstadt, Germany). Methanol (HPLC grade), NaOH (Analytical grade) and NaF (Analytical grade) were purchased from Merck (HPLC grade, Darmstadt, Germany). Phosphoric acid was obtained from Sigma-Aldrich (Steinheim, Germany). Stock solutions of Zr(IV) were prepared daily by appropriate dilution. A solution of 5-Br-PADAP in HPLC grade ethanol (Darmstadt, Germany). EDTA (Ethylenediamine tetraacetic acid) and EGTA (ethylene glycol tetraacetic acid) were purchased from Sigma (Steinheim, Germany). SPE cartridges (Waters, Milford, USA) were used for solid-phase extraction. All solutions were stored in a freezer at -20°C ready for use.

2.2. Sampling

Drinking water samples were taken from different provinces in Isparta and Burdur. Samples were transported to the laboratory, zirconium and fluoride analyses were performed immediately after the water. Bottled water samples of different brands were purchased from local markets.

2.3. Analysis of the Real Samples

A 100 mL of tap water and bottled water samples were filtered through 0.45μm membrane filter. For the analysis of water samples, solid phase extraction method was used. Sample was passed through a SPE cartridge previously conditioned by passage of 5 mL methanol and 3 mL ultrapure water, avoiding dryness. Then, the prepared sample was allowed to percolate slowly through the activated SPE cartridge at a flow rate approximately 8-10 mL/min. After loading the sample, cartridges were washed with 10 mL ultrapure water. The cartridge was dried by passage of air by use of a vacuum for 15 min and then ternary chelates of fluoride were elueted with three times by 0.5 ml of H_2O/Methanol (25/75, v/v) containing $5.00.10^{-6}$ mol/L of zirconium and $5.00.10^{-5}$ mol/L of PADAP. Zirconium chelates were obtained with H_2O/Methanol (25/75, v/v) containing $7.5.00.10^{-5}$ mol/L of PADAP (Oszwadowski et al. 1998, Oszwaldowski and Jakubowska 2003).

2.4. HPLC Analysis

High Performance liquid chromatography system was used to determine the zirconium and fluoride concentrations in drinking water, and bottled water samples. For analysis, detection and quantification were carried out with Shimadzu CBM-20A (Kyoto, Japan), LC-10AT pump, CTO-10ASvp column oven, SIL-20AC HT Autosampler and SPD-M10Avp (Diode Array Detector). The Phenomonex Luna C8 kolon (150 x 4.6 mm I.D; 5µm) column was used. The mobile phase consisted of H_2O/Methanol (25/75, v/v) at a flow rate of 1.0 ml/min with isocratic elution and the injection volume was 20 µl. The pH of the mobile phase containing 50 mM phosphoric acid and adjusted 3.0 by the addition of sodium hydroxide (Secilmis et al. 2004).

2.5. Statistical Analyses

Data are expressed as mean ± SD. Limit of detection (LOD), limit of quantification (LOQ), linearity of calibration, intra-and inter-day accuracy, precision and recovery were estimated for the validation of this method. Each Zr and fluoride concentration were measured in five replicates. We defined the LOD as three times the background noise of the chromatographic instrument. Samples with amount below the LOD were not detectable. The extraction recovery and intraday precision of this method were determined by spiking water with Zr and fluoride in five replicates; they were extracted as previously described. The inter-day precision and recovery were assessed by analyzing the target Zr and fluoride spiked at 5 different days.

3. Results

3.1. Optimization of the System

In the literature, EDTA and EGTA have been used in other studies. In this study, EDTA and EGTA were tested for the mobile phase optimization. Therefore, it is used for optimization studies. However, the peaks are suppressed and reduced these verity of peak or no peak could be obtained. Best results were obtained using the pH of the mobile phase containing 50 mM phosphoric acid and adjusted 3.0 by the addition of sodium hydroxide.

3.2. Detection Limit and Accuracy

The detection limit of zirconium (LOD) was 0.4 µg/L (3*sb*=*b*). The detection limit of (LOD) fluoride was 0.015 µg/L (3*sb*=*b*) in the method. Where *sb* is the standard deviation of the blank determinations and *b* isthe slope of the calibration curve.

3.3. Recovery

Multi-level calibration curves (r=0.999 for Zr; r= 0.999 for fluoride) were created for the quantification by using standard solutions in H_2O/Methanol (25/75, v/v). In validation studies, the average recovery values based on the spiked samples at five different zirconium levels were 99.74-100.17% and 100.05-104.33% for tap water and bottled water, respectively (Table 1). The average recovery values based on the spiked samples at 3 different fluoride levels were 93.33-103.33% and 102.86-106.67% for tap water and bottled water, respectively (Table 2).

Table 1. Avarage recovery values for Zr.

Source	Zr added (µg/L)	Zr found (µg/L)	RSD (%)	Avarage Recovery , %
Tap water	90.00	90.15	0.6	100.17
Tap water	110.00	110.08	0.3	100.07
Tap water	190.00	189.95	0.7	99.74
Bottled water	30.00	30.13	0.9	104.33
Bottled water	110.00	110.98	0.6	100.89
Bottled water	190.00	190.10	0.8	100.05

Table 2. Avarage recovery values for fluoride.

Source	F added (µg/L)	F found (µg/L)	RSD (%)	Recovery (%)
Tap water	15	14	0.5	93.33
Tap water	30	31	0.3	103.33
Tap water	70	68	0.6	97.14
Bottled water	15	16	0.8	106.67
Bottled water	30	1	0.5	103.33
Bottled water	70	72	0.7	102.86

Table 3. Intra-day and inter-day precisions for Zr.

Component	Precision Intraday (n=5) (µg/L)			Precision Inter-Day (n=5) (µg/L)		
	75.00	110	250.00	75.00	110	250.00
Zr	75.11	110.05	250.02	74.92	109.98	249.97

Table 4. Intra-day and inter-day precisions for fluoride.

Component	Precision Intraday (n=5) (µg/L)			Precision Inter-Day (n=5) (µg/L)		
	5.00	30.00	95.00	5.00	30.00	95.00
Fluoride	5.05	31.03	95.22	4.95	29.04	95.04

Intra and inter-day precisions are shown in Table 3 and Table 4.

The optimized method was succesfully applied to the determination of Zr. Working water samples did not contain Zr. Therefore, several spiked samples were prepared by adding aliquots (a few micro litres) for Zr solution to tap and bottled water samples and the effect of matrix and interfering species were investigated. Results show that this method has good accuracy and it is applicable for routine measurements.

3.4. Application of the Method

The proposed method was succesfully applied to the determination of fluoride. It was applied to several real samples including, tap water (Isparta and Burdur) and bottled water samples of different brands were purchased from local markets.

Fourty tap water samples were examined for fluoride content. The ion fluoride concentration in tap water is shown in Table 5. The highest concentration found was 1.20 mg/L in the water and the lowest level of fluoride was found 0.087 mg/L. Flouride was not detected in some tap water samples (tap water 36 and tap water 40).

Sixteen bottled water samples were examined for fluoride content. The ion fluoride concentration in bottled water is shown in Table 6. The highest concentration found was 0.094 mg/L in the water and the lowest level of fluoride was found 0.011 mg/L. Fluoride was not detected in some botted water samples (bottled water 6, bottled water 7, bottled water 9, and bottled water 10).

Currently, the US EPA has set an applicable maximum contaminant level for fluoride at 4 mg/L, with a maximum contaminant level goal at 4 mg/L under National Primary Drinking Water Regulations. Also, the US EPA has set a secondary maximum contaminant level for fluoride at 2 mg/L, with a maximum contaminant level goal at 2 mg/L under National Secondary Drinking Water Regulations. The World Health Organization (WHO) also sets a guideline value of 1.5 mg/L for fluoride in drinking waters. Tap water and bottled water fluoride concentration level values are below the specified values.

4. Discussion

Considering that HPLC equipment is a classic apparatus found in experimental laboratories, the developed method of Zr and fluoride determination can be thought of as an easily accessible alternative to other instrumental methods (Table 7).

Table 5. The ion fluoride concentration in tap water.

Source	F (Mean ± SD) (mg/L)
Tap water 1	0.251 ± 0.011
Tap water 2	0.110 ± 0.015
Tap water 3	1.131 ± 0.008
Tap water 4	0.350 ± 0.010
Tap water 5	0.123 ± 0.014
Tap water 6	0.253 ± 0.010
Tap water 7	0.154± 0.013
Tap water 8	0.210 ± 0.010
Tap water 9	0.174 ± 0.016
Tap water 10	0.258 ± 0.015
Tap water 11	0.175 ± 0.014
Tap water 12	0.199 ± 0.011
Tap water 13	0.360 ± 0.012
Tap water 14	0.650 ± 0.009
Tap water 15	0.357 ± 0.010
Tap water 16	0.578 ± 0.013
Tap water 17	0.404 ± 0.016
Tap water 18	0.499 ± 0.012
Tap water 19	0.998 ± 0.009
Tap water 20	0.298 ± 0.012
Tap water 21	1.205 ± 0.007
Tap water 22	0.224 ± 0.022
Tap water 23	0.589 ± 0.012
Tap water 24	1.252 ± 0.009
Tap water 25	1.101 ± 0.008
Tap water 26	0.287 ± 0.015
Tap water 27	0.854 ± 0.010
Tap water 28	0.158± 0.018
Tap water 29	0.289 ± 0.013
Tap water 30	0.228 ± 0.012
Tap water 31	0.418 ± 0.013
Tap water 32	0.113 ± 0.022
Tap water 33	0.134± 0.019
Tap water 34	0.150± 0.018
Tap water 34	0.102± 0.018
Tap water 36	ND
Tap water 37	0.019 ± 0.041
Tap water 38	0.095 ± 0.031
Tap water 39	0.087 ± 0.033
Tap water 40	ND

***ND:** not detected.*

The developed method is an alternative to the Zr determination by the, UV/Vis, AAS or ICP. Detection limit values are similar to the work done by, UV/Vis, AAS or ICP (Shariati and Yamini 2006, Zaporozhets and Ye Tsyukalo 2007, Afzali et al. 2014, Amin 2015). Also, the developed method is an alternative to the fluoride determination by

Table 6. The ion fluoride concentration in bottled water.

Source	F (Mean ± SD) (mg/L)
Bottled water 1	0.011± 0.022
Bottled water 2	0.094± 0.010
Bottled water 3	ND
Bottled water 4	0.015± 0.020
Bottled water 5	0.020± 0.019
Bottled water 6	ND
Bottled water 7	ND
Bottled water 8	0.035± 0.013
Bottled water 9	ND
Bottled water 10	ND
Bottled water 11	0.028± 0.018
Bottled water 12	0.011± 0.031
Bottled water 13	0.072± 0.011
Bottled water 14	0.011± 0.025
Bottled water 15	0.022± 0.018
Bottled water 16	0.019± 0.020

***ND:** not detected.*

Table 7. Current methods for fluoride analysis of drinking water.

Techniques	Standard Methods
Ion-Selective Electrode	EPA 340.2
	OSW 9214
	ASTM D1179-93B
	Standard Methods 4500FC
Ion Chromatography	EPA 300.00, EPA 300.1
	OSW 9056A
	ASTM D4327-91
	Standard Methods 4110B
Colorimetry	EPA 340.1, EPA 340.3
	Standard Methods 4500FD

the ion chromatography, spectrophotometry or ions elective electrodes because there are used only a conventional equipment (HPLC), not require derivization and detection limit is sufficient (Gleisner et al. 2011, Wejnerowska et al. 2007, Tokalioglu et al. 2001, Musijowsk et al. 2010, Koblar et al. 2012, Marques and Coelho 2013). The detection limits are standard methods in the range between 0.5 mg/L 0.005 mg/L.

One of the most important sources of water consumption in babies and children is the tap water and bottled water and the level off fluoride to both preventing of dental caries and fluorosis is an important factor. Lack of fluoride in children nutrition can lead to failing of healthy teeth and bones production, whereas fluorosis is an chronic disease that due to excess fluoride up take and exhibit with mottling and yellowish or brownish teeth. In addition to tap water, bottled water is used too much in Burdur and Isparta.

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