Feasibility of using Total Reflection X-ray Fluorescence Spectrometry for Drinking Water Analysis

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The quantitative elemental measurements in drinking water are a very important task since Brazilian legislation establishes the threshold limit value for each element. Besides Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) have been routinely used for this purpose, Total Reflection X-ray Fluorescence spectrometry (TXRF) seems to be a very interesting alternative. It provides a fast and easy sample preparation, low analytical operation and maintenance costs. This study shows the feasibility of using TXRF for monitoring simultaneously the presence of arsenic, barium, lead, copper, chromium, nickel, selenium, uranium, iron, manganese and zinc in drinking water samples. All measurements were performed using TXRF spectrometer, equipped with an air cooled low power X-ray tube (Mo target). For internal calibration, 950 μL of sample was mixed with 50 μL of a standard solution containing 10 mg L^{-1} of gallium. For most of the elements, the direct quantification by TXRF using Ga as internal standard could be used. For the Cr, Ni and U measurements, analytical calibration curves have to be adopted. The limits of detection for proposed method are appropriate for all elements investigated. In addition, the method showed good precision and accuracy and seems to be a very interesting alternative to be used in the routine analysis involving elemental measurement in drinking water samples analysis.

Keywords: drinking water, elemental analysis, TXRF

INTRODUCTION

Supply of safe drinking water is crucial to human life and safe drinking water should not impose a significant risk to humans [1]. Although a few elements are essential for human health, an excess amount of these metals can have negative effects. The Brazilian Drinking Water legislation provide the reference which defines safe, good quality water, how it can be achieved and how it can be assured. They are concerned with health safety aesthetic quality [2]. Inorganic species in drinking water usually occur as dissolved salts, especially carbonates, chlorides and sulfates. Inorganic compounds are generally present in water in concentrations substantially higher than organic compounds. Taste thresholds for some commonly occurring inorganic ions are about 0.1 mg L^{-1} for manganese, 0.3 mg L^{-1} for iron, 2 mg L^{-1} for copper, 5 mg L^{-1} for zinc, 250 mg L^{-1} for chloride, and 250-500 mg L^{-1} for sulfate. Most of these ions have health guidelines even at concentrations higher than their taste thresholds. However, in most cases the customer would reject the water for aesthetic reasons. Table I presents the Brazilian drinking water guideline value for the inorganic species [2].

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Table I. Brazilian drinking water guideline value (DMGV) for the inorganic species

Parameters	Element	DWGV* (mg L ⁻¹)
Toxic	Antimony	0.005
	Arsenic	0.01
	Barium	0.7
	Cadmium	0.005
	Lead	0.01
	Copper	2
	Chromium	0.05
	Nickel	0.07
	Selenium	0.01
	Uranium	0.03
Organoleptic	Aluminum	0.2
	Iron	0.3
	Manganese	0.1
	Zinc	5

Flame atomic absorption spectrometry (FAAS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) have been routinely used for water quality control. Besides the good performance of those methods and the adequate limits of detection for this purpose, the cost of analysis is high. The requirement of analytical grade gases (acetylene and argon) and high cost of consumables increase the cost of analysis. The total reflection X-ray fluorescence spectrometer used in this study, for example, is a plug and play system, compact with low energy consumption, completely independent of any cooling medium or exhaustion system, without the need for disposables or analytical grade gases, greatly reducing the cost of analysis. In this context, the use of Total Reflection X-ray Fluorescence spectrometry (TXRF) show to be a very interesting alternative. It provides fast and easy sample preparation processes and the costs of analytical operation and maintenance are low [3]. In this technique, X-ray is focused onto the sample and its energy is able to excite the atoms and induce the emission of fluorescence radiation, which is specific for each element. At very shallow angles of incidence of the exciting X-rays with respect to a flat specimen surface, external total reflection of the incident radiation occurs and drastically reduces the penetration depths of the incident radiation into the specimen bulk, thus enhancing the surface sensitivity by decreased substrate fluorescence and scattered excitation radiation intensities. During the last few decades this Total-reflection XRF (TXRF) method became one of the faster and lower cost competitive techniques for trace element analyses [4].

Radiation sources commonly used in TXRF is made with the molybdenum or tungsten. Each of them has a useful range for the determination and quantification of the elements present in the samples. The molybdenum source shows a useful range between 3 and 15 keV. For this reason, elements whose emission of fluorescence is near the extremes of this range cannot be quantified. In this condition, Al can be detected, but its quantification is compromised due to the interference caused by Si and Ar. In another situation, elements like Cd and Sb are subject to spectral interference by molybdenum coming from the tube. To minimize the spectral interference allowing the quantitative measurement of low energy elements, the use of TXRF instrument equipped with an air cooled low power X-ray tube (W target) and monochromator with signal amplifier is recommended [5].

In recent years, TXRF has been used in elemental measurement in water samples. Riaño et al. developed a practical and easy guideline for the correct preparation of aqueous samples, showing the effect of different parameters as measurement time, carrier position, sample volume and sample drying time [6]. Floor et al. assessed the components contributing to the combined uncertainty budget associated

with TXRF measurements using Cu and Fe concentrations in different spiked and natural water samples [7]. Romero et al. developed a headspace thin-film microextraction onto graphene membranes for specific detection of methyl(cyclopentadienyl)-tricarbonyl manganese in water samples and the reflectors containing graphene membranes were directly used as sample carriers for TXRF analysis [8,9]. Woelfl et al. determined Cr, Mn, Fe, Ni, Cu, Zn, As and Pb in freshwater rotifers and ciliates by TXRF spectrometry [10]. Bahadir et al. proposed a method to preconcentration and determination of Cr species in water samples, and another methodology based on the combination of dispersive microsolid-phase extraction (DMSPE) with total reflection X-ray fluorescence (TXRF) spectrometry for the determination of hexavalent chromium in drinking waters [11,12].

This work proposes evaluate the feasibility to use the total reflection X-ray fluorescence spectrometry for monitoring the presence of metals presented in Table I, with the exception of Al, Cd and Sb, by multi-elemental direct determination in drinking water samples, attending the parameters established by Brazilian legislation.

MATERIALS AND METHODS

Instruments

All measurements were performed using a benchtop S2 PICOFOX TM TXRF – spectrometer (Bruker Nano GmbH, Karlsruhe, Germany) equipped with a Mo tube – K α 17.5 keV excitation source (600 mA, 50 kV, 50 W), a multi-layer monochromator and a silicon drift detector with an active area of 10 mm². The resolution of the detector was better than 160 eV at 10 kpcs (MnK α). The X-ray tube is provided with a primary radiation protection made of 5 mm-brass, a thin Beryllium window (100 μ m) by which the X-rays escape to the outside. In the direction to the monochromator a 3 mm-opening for the emission of the useful beam is provided. Sample carriers made of synthetic quartz glass. The measurement time was 600 s per sample. The processing of the X-ray spectra and the accounting for fluorescence peak overlaps were performed using the software SPECTRA version 7.0 (Bruker Nano GmbH, Karlsruhe, Germany).

The analytical results obtained with the TXRF spectrometer were cross-checked with results obtained by ICP OES Thermo Scientific™ iCAP™ 7400 (Thermo Scientific, China) with dual view configuration and multichannel CCD array detector.

An analytical balance (Mettler Toledo, Switzerland) was employed for weighing samples and a vortex shaker (Scientific Industries, USA) to homogenize the samples. An electronic pipette (Rainin/Mettler Toledo, USA) was employed to transfer the sample aliquot to quartz disk. A dry oven (Ethik Technology, Brazil) was employed to dry the samples aliquot.

Reagents and samples

All analytical solutions were prepared with high purity deionized water obtained from a Milli-Q water purification system (Millipore, USA) and stored in decontaminated polypropylene tubes (Aton, USA) and all samples were stored in microtubes of 2.0 mL (Aton, USA).

Standards solutions containing 1000 mg L⁻¹, produced by laboratories with ISO 17025, ISO Guide 34 accreditation and NIST traceability (Table II), were added over real water samples and used to check the accuracy of the analytical method developed. The 1000 mg L⁻¹ gallium (Ga) standard solution was obtained from Inorganic Venture (Christiansburg, USA). A silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany).

Table II. NIST traceability of the standards solutions

Element	Stock standard solutions(1000 mg L ⁻¹)	NIST traceability
Arsenic	Inorganic Ventures - K2-AS650402	NIST SRM 3103a
Barium	SPC Science - S161003016	NIST SRM 3104a
Lead	Inorganic Ventures - K2-PB03074	NIST SRM 3128
Copper	Absolute Standard, Inc-060515	NIST SRM 3114
Chromium	Inorganic Ventures - J2-CR03111	NIST SRM 3112a
Nickel	Inorganic Ventures - J2-NI02103	NIST SRM 3136
Selenium	Inorganic Ventures - J2-SE02058	NIST SRM 3149
Uranium	Inorganic Ventures - J2-U01107R	NIST SRM 3164
Iron	Absolute Standard, Inc-102815	NIST SRM 3126a
Manganese	Ultra Scientific - P01081 Inorganic	NIST SRM 3132
Zinc	Ventures - J2-ZN	NIST SRM3103a

Procedure

Sample carriers were pretreated with 5 µL of silicone in isopropanol at room temperature and dried for 15 min in a drying oven at 60 °C. This procedure was followed to make the surface hydrophobic and avoid spreading of the aqueous sample on the carrier.

For internal calibration, 950 µL of sample was mixed with 50 µL of a standard solution (Ga; 10 mg L⁻¹). For the measurement, a volume of 5 µL of the sample was added onto the carrier at room temperature and dried at 60 °C in a drying oven for 15 min. This procedure was performed three times to preconcentrate the samples. The gain correction was done before starting the analysis. Samples were measured for 600 s. The optimization of the instrumental parameters was performed according to the preparation of aqueous samples proposed by Riano et al. which involves 15 min for silicone in isopropanol drying time and 600 s for measurement time [6]. Spectra were analyzed with the Bruker Spectra Picofox version 7.5.3.0 software and the limits of detection were calculated by the same software. This software use the 3-sigma criterion to calculate the limits of detection. As the elements are identified and quantified by means of their fluorescence peaks, the definition of the detection limits is based on a statistical inspection of the peak area and the subjacent spectral background. Thereby, it is assumed that an element is considered to be detected if the peak area is three times larger than as the counting statistics of the background (Equation 1).

$$LLD_i = \frac{3 \cdot C_i \cdot \sqrt{N_{BG}}}{N_i} \quad (\text{Equation 1})$$

with the meaning

LLD_i lowest limit of detection of the element i in milligrams per liter

C_i concentration of the element i in milligrams per liter

N_i area of the fluorescence peak in counts

N_{BG} background area subjacent the fluorescence peak in counts

The quantification limits were calculated according to CGCRE 008 of Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO) (Equation 2) [13].

$$LQ_i = LLD_i + 5 \cdot s_i \quad (\text{Equation 2})$$

Article

with the meaning

LQ_i limit of quantification of the element i

LLD_i lowest limit of detection of the element i

s_i standard deviation of lowest limit of detection of the element i

The results obtained by the proposed method were compared with those obtained by the conventional method using ICP OES in which the sample was analyzed directly without any dilution. The wavelengths (nm) used for each element were: As (189.042), Ba (455.403), Cd (228.802), Pb (220.353), Cu (324.754), Cr (283.563), Fe (259.940), Mn (257.610), Ni (341.476), Se (196.090), U (409.014) e Zn (213.856). The measurements were performed using axial view, 2 L min⁻¹ of plasma gas flow, 1200W RF power and concentric nebulizer.

RESULTS AND DISCUSSION

All experiments were performed using Ga as internal standard which is the most common element used in TXRF measurements and it is rarely found in drinking water samples. Figure 1 shows the TXRF spectrum of a spiked drinking water sample using Ga as internal standard for quantification of each analyte.

Figure 1. TXRF spectrum of a spiked drinking water sample

Table III shows the results obtained for direct analysis of the drinking water using Ga 0.5 mg L⁻¹ as internal standard.

Table III. Limits of quantification and results obtained for direct analysis of the drinking water by TXRF using 0.5 mg L⁻¹ of Ga as internal standard

Element	LQ* (mg L ⁻¹)	Drinking water samples(mg L ⁻¹)	Spike (mg L ⁻¹)	Drinking water spiked samples (mg L ⁻¹)	Recovery (%)
Arsenic	0.003	0.007±0.001	0.01	0.035±0.001	106
Barium	0.002	<0.002	0.7	0.64±0.03	91
Lead	0.005	<0.005	0.01	0.009±0.001	90
Copper	0.029	0.006±0.001	2	2.02±0.14	100
Chromium	0.005	<0.005	0.05	0.044±0.014	88
Nickel	0.006	<0.006	0.07	0.065±0.005	87
Selenium	0.003	<0.003	0.01	0.010±0.001	98
Uranium	0.003	<0.003	0.03	0.025±0.001	83
Iron	0.02	0.840±0.008	0.3	1.19±0.02	103
Manganese	0.02	0.170±0.009	0.1	0.28±0.02	101
Zinc	0.76	0.120±0.007	2	2.05±0.14	96

*Limit of Quantification

Considering the threshold limits established by the legislation (Table I), limits of quantification for the proposed method (Table III) show to be appropriate. As the concentration of As, Ba, Pb, Cu, Cr, Ni, Se, U, Fe, Mn and Zn were lower than the limit of detection of the method, addition and recovery test was performed to check the matrix interference. The concentration used for spiking was based on Brazilian drinking water guideline value (Table I). For most analytes, recoveries between 83 and 106% (Table III) were obtained, indicating the absence of significant matrix interference in the direct analysis of drinking water by TXRF. For the analytes Cr, Ni and U, the recoveries were lower than 90% at different concentrations showed in Figure 2. To improve the analytical results, analyses were performed using analytical calibration curves (Figure 2) instead of using direct methods which involves the use of Ga as internal standard. Addition and recovery tests were also performed and the obtained results were compared to those obtained by using direct methods (Figure 3).

Figure 2. Analytical calibration curves in deionized water for TXRF analysis for Cr (a), Ni (b) and U (c)

Figure 3. Recoveries values for analysis made using direct method and method using analytical calibration curve for Cr, Ni and U

Figure 3 shows that the recoveries for Cr, Ni and U were improved when analysis were done using calibration methods showing that for these elements the quantification using Ga as internal standard was not enough. For this reason, for those elements, calibration curves were adopted for analysis.

The direct quantification of Cr, Ni and U by the internal standard would be possible by altering the constants of these analytes in the equipment software. The constants correspond to the slope (Sl_i) in a plot of the net counts of the element peak versus the net counts of the Ga peak multiplied by concentration of the element divided by concentration of Ga solution. Sl_i is determined by the Equation 3 and it is a part of the Equation 4, used to determine the concentration of the analyte. As the software doesn't allow the access to change the constants, the external calibration was performed through the analytical curve, correcting the results mathematically.

$$Sl_i = \frac{N_i \cdot C_{Ga}}{N_{Ga} \cdot C_i} \quad (\text{Equation 3})$$

with the meaning

Sl_i sensitivity of the element i in milligrams per liter

N_i element i peak in net counts

C_{Ga} concentration of Ga solution in milligrams per liter

N_{Ga} Ga peak in net counts

C_i concentration of the element i in milligrams per liter

$$C_i = \frac{C_{Ga} \cdot N_i \cdot S_{Ga}}{N_{Ga} \cdot Sl_i} \quad (\text{Equation 4})$$

with the meaning

C_i concentration of the element i in milligrams per liter

C_{Ga} concentration of Ga in milligrams per liter

N_i element i peak in net counts

S_{Ga} sensitivity of Ga in milligrams per liter

N_{Ga} Ga peak in net counts

Sl_i sensitivity of the element i in milligrams per liter

Using the proposed method, drinking water samples were analyzed by TXRF method and the results obtained by the proposed method were compared to those obtained by ICP OES technique (Table IV).

Table IV. Results obtained for direct analysis of drinking water samples by ICP OES and by TXRF

Element	Sample	Results TXRF (mg L ⁻¹)	Spike (mg L ⁻¹)	TXRF (mg L ⁻¹)	REC (%)	ICP OES (mg L ⁻¹)	REC (%)
Arsenic	A – 1*	<0.003	0.01	0.0097 ± 0.0004	97	0.0107 ± 0.0005	107
	A – 2*	<0.003		0.0102 ± 0.0005	102	0.0103 ± 0.0006	103
	A – 3*	<0.003		0.0099 ± 0.0003	99	0.0101 ± 0.0006	101
	B – 1**	<0.003		0.0104 ± 0.0006	104	0.0099 ± 0.0007	99
	B – 2**	<0.003		0.0101 ± 0.0005	101	0.0104 ± 0.0006	104
	B – 3**	<0.003		0.0103 ± 0.0006	103	0.0101 ± 0.0005	101
Barium	A – 1*	0.353 ± 0.021	0.7	1.061 ± 0.184	98	1.116 ± 0.044	106
	A – 2*	0.501 ± 0.017		1.191 ± 0.175	102	1.321 ± 0.124	110
	A – 3*	0.575 ± 0.033		1.299 ± 0.027	96	1.173 ± 0.116	92
	B – 1**	0.356 ± 0.023		1.067 ± 0.089	97	1.066 ± 0.111	101
	B – 2**	0.368 ± 0.016		1.061 ± 0.163	102	1.153 ± 0.096	108
	B – 3**	0.468 ± 0.022		1.150 ± 0.052	104	1.203 ± 0.065	103
Lead	A – 1*	<0.005	0.01	0.0101 ± 0.0006	101	0.0103 ± 0.0005	103
	A – 2*	<0.005		0.0104 ± 0.0005	104	0.0100 ± 0.0006	100
	A – 3*	<0.005		0.0098 ± 0.0006	98	0.0101 ± 0.0007	101
	B – 1**	<0.005		0.0096 ± 0.0006	96	0.0096 ± 0.0007	96
	B – 2**	<0.005		0.0103 ± 0.0005	103	0.0101 ± 0.0006	101
	B – 3**	<0.005		0.0102 ± 0.0006	102	0.0098 ± 0.0004	98
Copper	A – 1*	0.052 ± 0.003	2	2.093 ± 0.051	102	2.011 ± 0.056	98
	A – 2*	0.034 ± 0.004		2.095 ± 0.063	103	2.014 ± 0.071	99
	A – 3*	0.061 ± 0.002		2.205 ± 0.152	107	2.061 ± 0.023	100
	B – 1**	0.070 ± 0.003		2.091 ± 0.053	101	2.029 ± 0.052	98
	B – 2**	0.057 ± 0.003		2.139 ± 0.075	104	2.078 ± 0.034	101
	B – 3**	0.031 ± 0.002		2.072 ± 0.051	102	2.072 ± 0.063	102
Chromium	A – 1*	<0.005	0.05	0.052 ± 0.003	104	0.055 ± 0.006	110
	A – 2*	<0.005		0.054 ± 0.004	108	0.054 ± 0.006	108
	A – 3*	<0.005		0.051 ± 0.003	102	0.051 ± 0.001	102
	B – 1**	<0.005		0.051 ± 0.003	102	0.049 ± 0.002	98
	B – 2**	<0.005		0.053 ± 0.003	106	0.053 ± 0.003	106
	B – 3**	<0.005		0.053 ± 0.003	106	0.052 ± 0.003	104
Nickel	A – 1*	<0.006	0.07	0.075 ± 0.006	107	0.072 ± 0.003	103
	A – 2*	<0.006		0.075 ± 0.005	107	0.072 ± 0.004	103
	A – 3*	<0.006		0.077 ± 0.007	110	0.067 ± 0.005	96
	B – 1**	<0.006		0.071 ± 0.004	101	0.067 ± 0.004	96
	B – 2**	<0.006		0.072 ± 0.005	103	0.070 ± 0.002	100
	B – 3**	<0.006		0.075 ± 0.006	107	0.067 ± 0.005	96
Selenium	A – 1*	<0.003	0.01	0.0099 ± 0.0003	99	0.0102 ± 0.0003	102
	A – 2*	<0.003		0.0101 ± 0.0002	101	0.0098 ± 0.0004	98
	A – 3*	<0.003		0.0100 ± 0.0002	100	0.0099 ± 0.0002	99
	B – 1**	<0.003		0.0106 ± 0.0007	106	0.0096 ± 0.0005	96
	B – 2**	<0.003		0.0103 ± 0.0005	103	0.0102 ± 0.0004	102
	B – 3**	<0.003		0.0097 ± 0.0005	97	0.0103 ± 0.0005	103
Uranium	A – 1*	<0.003	0.03	0.028 ± 0.003	93	0.030 ± 0.001	100
	A – 2*	<0.003		0.031 ± 0.002	103	0.030 ± 0.002	100
	A – 3*	<0.003		0.032 ± 0.003	107	0.033 ± 0.003	110
	B – 1**	<0.003		0.029 ± 0.003	97	0.031 ± 0.003	103
	B – 2**	<0.003		0.029 ± 0.002	97	0.028 ± 0.003	93
	B – 3**	<0.003		0.033 ± 0.003	110	0.032 ± 0.003	107
Iron	A – 1*	0.066 ± 0.005	0.3	0.384 ± 0.021	105	0.366 ± 0.008	100
	A – 2*	0.054 ± 0.006		0.361 ± 0.012	102	0.350 ± 0.011	99
	A – 3*	0.087 ± 0.006		0.391 ± 0.011	101	0.391 ± 0.012	101
	B – 1**	0.101 ± 0.007		0.413 ± 0.015	103	0.409 ± 0.015	102
	B – 2**	0.096 ± 0.005		0.412 ± 0.021	104	0.388 ± 0.023	98
	B – 3**	0.053 ± 0.004		0.374 ± 0.026	106	0.357 ± 0.021	101

Table IV. Results obtained for direct analysis of drinking water samples by ICP OES and by TXRF (cont.)

Element	Sample	Results TXRF (mg L ⁻¹)	Spike (mg L ⁻¹)	TXRF (mg L ⁻¹)	REC (%)	ICP OES (mg L ⁻¹)	REC (%)
Manganese	A – 1*	0.023 ± 0.001	0.1	0.134 ± 0.021	109	0.125 ± 0.009	102
	A – 2*	0.031 ± 0.001		0.138 ± 0.015	105	0.128 ± 0.008	98
	A – 3*	0.022 ± 0.003		0.129 ± 0.013	106	0.123 ± 0.009	101
	B – 1**	0.061 ± 0.003		0.166 ± 0.014	103	0.164 ± 0.007	102
	B – 2**	0.033 ± 0.003		0.138 ± 0.011	104	0.137 ± 0.011	103
	B – 3**	0.041 ± 0.001		0.144 ± 0.008	102	0.142 ± 0.009	101
Zinc	A – 1*	0.152 ± 0.009	2	2.109 ± 0.097	98	2.238 ± 0.022	104
	A – 2*	0.201 ± 0.012		2.267 ± 0.128	103	2.333 ± 0.087	106
	A – 3*	0.269 ± 0.016		2.360 ± 0.122	104	2.292 ± 0.023	101
	B – 1**	0.129 ± 0.011		2.065 ± 0.022	97	2.172 ± 0.031	102
	B – 2**	0.116 ± 0.009		2.010 ± 0.097	95	2.074 ± 0.042	98
	B – 3**	0.154 ± 0.011		2.176 ± 0.088	101	2.219 ± 0.061	103

* A = Drinking water treatment system sample

** B = Drinking water distribution system sample

Results from Table IV show that the values obtained by TXRF are in accordance with the results obtained by ICP OES, according to t-Test (95%) realized using the statistic function of Excel. Limits of quantification for TXRF and ICP OES presented in the Table V show that for the values obtained for Cu, Cr, Ni and Zn were higher for TXRF probably due to the less efficient X-ray fluorescence excitation in those concentrations presents in drinking water samples [14]. Besides this, due to the simplicity and low cost of analysis, TXRF is strongly recommended for routine analysis of drinking water.

Table V: Limits of quantification (LQ) for direct analysis of the drinking water samples by TXRF and ICP OES

Element	LQ TXRF (mg L ⁻¹)	LQ ICP OES (mg L ⁻¹)
Arsenic	0.003	0.003
Barium	0.002	0.010
Lead	0.005	0.004
Copper	0.029	0.005
Chromium	0.005	0.002
Nickel	0.006	0.002
Selenium	0.003	0.007
Uranium	0.003	0.019
Iron	0.02	0.05
Manganese	0.02	0.01
Zinc	0.76	0.01

CONCLUSIONS

This study presented the feasibility of using total reflection X-ray fluorescence spectrometry for multielemental direct determination in drinking water samples. The technique presented a simple, fast and safe sample preparation with optimized measurement time, resulting in a method three times faster, with high analytical frequency for the elemental determination compared to ICP OES, considering sample preparation, measurement time and data analysis. Besides this, the total reflection X-ray fluorescence spectrometer used in this study is a plug and play system, compact with low energy consumption, completely independent of any cooling medium or exhaustion system, without the need for disposables or analytical grade gases, greatly reducing the cost of analysis. For most of the elements investigated, direct

quantification by TXRF using Ga as internal standard was used. For the Cr, Ni and U elements measurements, the use of analytical calibration curves are recommended. The limits of detection are appropriate for all elements investigated since they are below Brazilian drinking water guideline value. In addition, the method showed good precision and accuracy. Considering the simplicity of the proposed procedure associated to low cost of analysis, TXRF is strongly recommended for routine analysis of drinking water.

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