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Elemental content in deionized water by total-reflection X-ray fluorescence spectrometry

G. A. Tavares · E. Almeida · J. G. G. de Oliveira · J. A. Bendassolli · V. F. Nascimento Filho

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Abstract This study aimed to evaluate minor and trace elements in the water during different water purification steps of a deionized water production plant, located at CENA, by total-reflection X-ray fluorescence (TXRF) technique, using Ga as internal standard for elemental quantification. This approach was capable of determining Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb at concentrations higher than 40–100 μg L^{-1}, and for K, Ca, Sc, Ti, V and Sr at concentrations higher than sub mg L^{-1} in the water samples. TXRF spectrometer encompasses an X-ray tube with a Mo target with a Zr filter. The elemental characteristic X-rays were recorded by a Si(Li) semiconductor detector and the X-ray spectra deconvoluted by AXIL software.

Keywords TXRF · Deionized water · Water quality · Chemical analysis

Introduction

Water is the most common solvent in chemical laboratories. However, its high purity is very important for many research activities such as sample and analytical standard preparations, glassware and plasticware cleaning, microorganism culture medium preparing and so forth. There are many water purification systems available, highlighting distillation, reverse osmosis and ion exchange through resin processes. Although distillation is a widespread and quite common water purification system, this process requires a large amount of water for cooling (10–20 L L^{-1}) and also energy for heating (0.7 kW L^{-1}) [1]. Reverse osmosis requires around 3 L L^{-1}; however, it is an energy saving process.

Among many techniques used in water purification, the use of ion exchange resin is very effective because of the resin durability, its simplicity, effective ion removal, and it is a water and energy saving process [2, 3].

In 2001, a deionized water production plant that uses ion exchange process was built at CENA/USP (Center for Nuclear Energy in Agriculture/University of São Paulo), Piracicaba, São Paulo State [4]. The main goal of this plant was to provide deionized water to all CENA laboratories. This plant is able to produce 100 L h^{-1} of deionized water. Compared to distillation (previous purified water system used at CENA), it is possible to save up to US$ 50,000 per year through the ion exchange process (available nowadays), taking into account the energy and water saving. Although the deionized water pH and conductivity are verified daily, a wider water quality monitoring is justified.

The TXRF technique is used for chemical micro and trace analyses and it is a variation of EDXRF [5]. In this analytical technique, a small quantity of a solution (5–50 μL) or suspension is pipetted onto optical flats, e.g., quartz glass. After a drying step, the residue is excited under a fixed small glancing angle and the X-ray characteristic radiations are recorded by a semiconductor detector, e.g. Si(Li), giving an energy dispersive spectrum.

This variant technique has several advantages over conventional EDXRF: (1) being the incident angle of the primary radiation below the critical angle, almost all of the incident photons are reflected, so the primary radiation barely penetrates into the reflector and the background from scattering on the substrate is highly reduced; (2) the sample is

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G. A. Tavares (✉) · E. Almeida · J. G. G. de Oliveira ·
J. A. Bendassolli · V. F. Nascimento Filho
Center for Nuclear Energy in Agriculture (CENA), University of São Paulo (USP), Av. Centenário, 303, Caixa Postal 96, CEP 13400-970 Piracicaba, SP, Brazil
e-mail: gtavares@cena.usp.br

double excited, by both the direct and the reflected beams; (3) due to the geometry, the detector is closed to the reflector surface where the sample is pippeted onto, and so it results in a large solid angle for detection. For that reasons, the TXRF peak-to-background ratio is elevated and the limits of quantification are several orders of magnitude improved in comparison to conventional EDXRF [5, 6].

In addition, TXRF has been applied in different sorts of water samples such as groundwater, tap, river and lake waters and so forth [5, 7–15]. Thus, TXRF was evaluated for routine analyses of water samples in order to determine the minor and trace elements during the different steps of CENA's deionized water production.

Experimental

Deionized water production system

In order to facilitate the access and transport of deionized water to all CENA laboratories, the plant of deionized water production through ion exchange process is located at the center of our Institute (Fig. 1). In the plant, a strong basic anion exchanger Amberlite IRA 410 Cl is utilized for anionic resin and a strong acid cation exchanger Amberjet 1200 Na for cationic resin is used. The production is a daily process; so, fresh deionized water is available all the time, and the conductivity and pH are monitored continuously.

Sampling

For this study, the sampling was carried out at four points at CENA's deionized water production plant: (P1) tap water from Piracicaba municipal water supply (input water), (P2) after sand and activated charcoal filtration bends, (P3) after anionic and cationic exchange resin percolation and UV sterilization process (output water), and (P4) after 5 day-storage in 304 stainless steel samples.

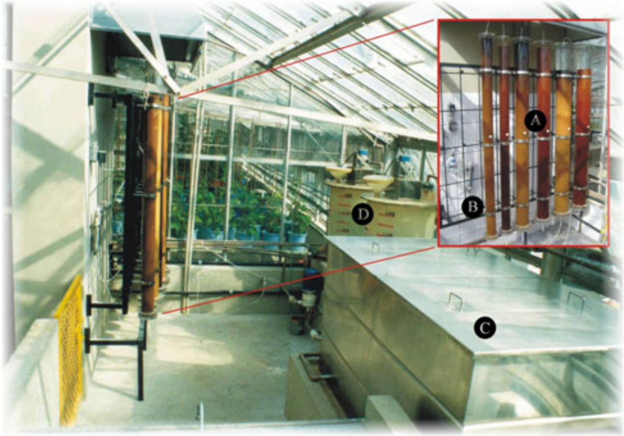

Fig. 1 CENA's deionized water production plant: **a** acrilic columns filled with anionic and cationic exchange resin; **b** Trojan UV-Max ultraviolet lamp; **c** 304 stainless steel tank for deionized water storage; **d** reservoirs for anionic and cationic exchange resin regenerative solution

Duplicate samples were collected and all samples were acidified at $\mathrm{pH} < 2$ (*pro analysi* HNO_3 65% purchased from Merck) and kept under refrigeration (4 °C) [16].

Analytical standards and sample preparations

Six multi-elemental analytical standards were prepared ranging from 0 to 10 $\mathrm{mg\,L^{-1}}$ for K, from 0 to 80 $\mathrm{mg\,L^{-1}}$ for Ca, and from 0 to 5 $\mathrm{mg\,L^{-1}}$ for Mn, Fe, Cu, Zn and Sr. These analytical standards were obtained from their 1000 $\mathrm{mg\,L^{-1}}$ stock analytical standards of Aldrich Inc. and Specsol brands. For quantitative elemental determination, Ga internal standard was used at 5.125 $\mathrm{mg\,L^{-1}}$. It was prepared from a Ga atomic absorption solution 1025 $\mathrm{\mu g\,L^{-1}}$ (Aldrich Inc.) through a proper dilution. For this study, 25 μL of the analytical standards was pipetted on to a 3.0 cm diameter quartz carrier and dried in a laboratory oven at 60 °C.

For TXRF sample preparation, 190 μL of sample and 10 μL of 102.5 $\mathrm{mg\,L^{-1}}$ Ga solution (from an 1:10 Ga 1025 $\mathrm{\mu g\,L^{-1}}$ stock solution dilution) were pippeted in a lock-top 1.5 mL microcentrifuge tube. After this, this solution was homogenized using a tube shaker (model 162, Marconi brand) and it was followed the same analytical standard analysis protocol. All procedures were carried out in a laminar flow chamber.

TXRF spectrometer

A TXRF module, produced by "Atominstitut der Österreichischen Universitäten", Vienna, Austria, consisting of a collimator unit, a 50 × 20 × 7 mm Duran cut-off reflector and a sample reflector holder. This was coupled to a fine-focus Mo X-ray tube with a Zr filter, operated at 30 kV and 40 mA. Acquisition time was 300 s for analytical standards and sample analyses.

The X-rays were recorded by a Si(Li) semiconductor detector, SL 80175 model, manufactured by Canberra. It was coupled to a preamplifier, amplifier and multichannel pulse analyzer card inserted in a microcomputer. The X-ray spectra were deconvoluted by AXIL software [17].

Elemental quantitative analyses

For TXRF quantitative analyses [7], the intensity of the analyte X-ray (I_i) is related to its concentration by Eq. 1:

$$R_i = S'_i C_i \tag{1}$$

in which

$$R_i = \frac{I_i}{I_{Ga}} C_{Ga} \quad (2)$$

and

$$S_i' = \frac{S_i}{S_{Ga}} \quad (3)$$

where R_i = relative intensity (µg mL^{-1}) and S'_i = relative sensitivity for element i; S_i and S_{Ga} = analytical sensitivities (cps mg^{-1} L); C_i and C_{Ga} = concentrations (mg L^{-1}); I_i and I_{Ga} = Kα line X-ray intensities (cps) for the elements i and Ga, respectively.

Limit of quantification

The limit of quantification LQ_i was calculated using Eq. 4 [7, 18]:

$$LQ_i = 10\sqrt{\frac{I_{i(BG)}}{t} \frac{C_{Ga}}{I_{Ga} S_i'}} \quad (4)$$

where LQ_i = limit of quantification (µg L^{-1}) and $I_{i(BG)}$ = background intensity of analyte i (cps); and t = acquisition time (s).

Results

Figure 2 shows the elemental relative sensitivity (R_i) dependence of atomic number (Z). Through this correlation, the relative sensitivity was determined for Sc, Ti, V, Cr, Co, Ni, Ge, As, Se, Br and Rb.

Figure 3 shows the *LQ* (mg L^{-1}) for elements from K (Z = 19) to Sr (Z = 38), except for Ga and Kr elements, taking into account the acquisition time of 300 s. It should be noted that *LQ* rises sharply for atomic number lower than 24. This is theoretically predicted in X-ray fluorescence for low atomic number elements due to both lower fluorescence yield, and air and Be window detector absorptions. To illustrate the TXRF analysis, P1 and P3 X-ray spectra can be seen in Fig. 4. Si, Ar and Ga characteristic X-ray peaks are due to their presences in the sample carrier (quartz), atmosphere and internal standard adding, respectively. Although it is difficult to visualize the increases of background for Z higher than 33 in Fig. 4, due to scale of this Figure, in fact, it rises significantly, because of the elastic and inelastic X-ray excitation scattering. Other feature is that the higher the X-ray energy, the lower is probability of interaction with the Si(Li) crystal in the detector. So, these two factor cause a worsening of the detection limit for Z higher than 33.

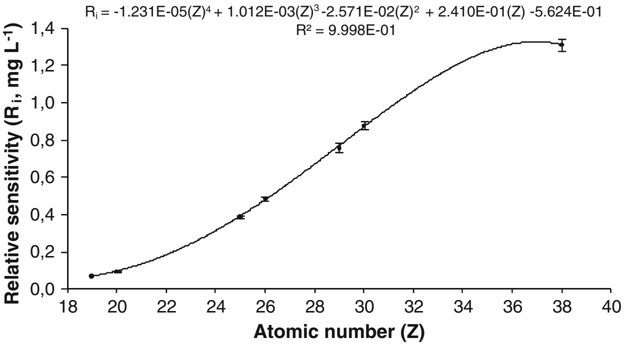

Fig. 2 Relative sensitivity (R_i) dependence of atomic number (Z)

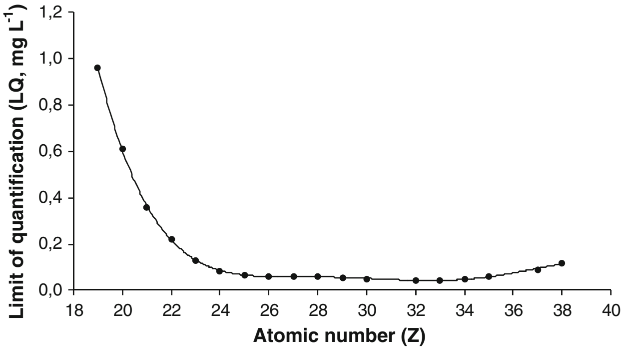

Fig. 3 Limits of quantification (*LQ*, mg L^{-1}) for elements K (Z = 19) to Sr (Z = 38), except for Ga and Kr

Table 1 presents the K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb and Sr concentrations (mg L^{-1}) in P1, P2, P3 and P4 samples. The *LQ* (mg L^{-1}) for these elements are shown on the right hand column of Table 1.

No significant differences were detected ($P < 0.05$, Student's *t* distribution) for K, Ca and Sr concentrations in P1 and P2 samples. It was expected because the sand bend and activated charcoal are not metal sorbents. On the other hand, Fe, Ni and Zn concentrations in P2 sample were 0.1, 0.1 and 0.5 mg L^{-1}, respectively. Although, these values were not expected because their concentrations in P1 sample were below *LQ*, it is possible that a Fe, Ni and Zn elution from sand and activated charcoal bends might have occurred on sampling, considering the duplicate was not collected at the same time, but in sequence. High relative standard deviations for these elements at P2 point are from their content differences in the replicates not due to TXRF analysis error.

The water supply agency of Piracicaba city provides a monthly water quality report [19]. Concerning the month of sampling, Fe and Mn concentrations were reported at 0.04 and 0.02 mg L^{-1}, respectively. These concentrations values are below their TXRF *LQ*s (Table 1). However, as far as TXRF monitoring is considered and these elements are below their TXRF *LQ*s, this purified water can be used directly for Mn and Fe determination in soil, plant and animal samples throughout, for example. Although, the

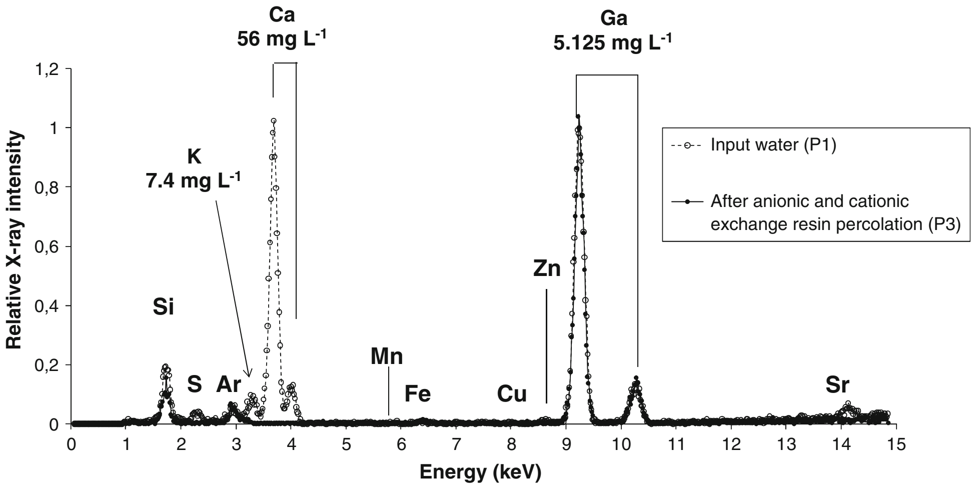

Fig. 4 X-ray spectra of water samples collected at two points at CENA's deionized water production plant (Si, Ar and Ga characteristic peaks are from the quartz glass sample carrier, atmosphere and internal standard, respectively)

Table 1 Concentrations (mg L^{-1}) of the elements from K to Sr in (P1) input water, (P2) after sand bend and activated charcoal filtration, (P3) after anionic and cationic exchange resin percolation and UV sterilization process (output water), and (P4) after 5 days storage in 304 stainless steel samples

Element	Samples				LQ[a]
	P1	P2	P3	P4	
K	5.5 ± 0.7	6 ± 1	<LQ	<LQ	0.96
Ca	46 ± 4	52 ± 5	<LQ	<LQ	0.61
Sc	<LQ	<LQ	<LQ	<LQ	0.36
Ti	<LQ	<LQ	<LQ	<LQ	0.22
V	<LQ	<LQ	<LQ	<LQ	0.13
Cr	<LQ	<LQ	<LQ	<LQ	0.082
Mn	<LQ	<LQ	<LQ	<LQ	0.068
Fe	<LQ	0.1 ± 0.1	<LQ	<LQ	0.061
Co	<LQ	<LQ	<LQ	<LQ	0.059
Ni	<LQ	0.1 ± 0.15	<LQ	<LQ	0.060
Cu	<LQ	<LQ	<LQ	<LQ	0.057
Zn	<LQ	0.5 ± 0.7	<LQ	<LQ	0.049
Ge	<LQ	<LQ	<LQ	<LQ	0.040
As	<LQ	<LQ	<LQ	<LQ	0.044
Se	<LQ	<LQ	<LQ	<LQ	0.050
Br	<LQ	<LQ	<LQ	<LQ	0.061
Rb	<LQ	<LQ	<LQ	<LQ	0.091
Sr	0.16 ± 0.03	0.18 ± 0.04	<LQ	<LQ	0.116

[a] Limit of quantification for 300 s counting time

CENA's tap water is from a Piracicaba's water treatment plant, in which metal levels might be altered compared to the Corumbataí river water (from which mostly Piracicaba's city tap water comes from), it is not rare to face Mn and Fe concentrations at hundreds μg L^{-1} or even at mg L^{-1} level in natural waters. Moreover, some Piracicaba city's pipes are Fe-based material ones in which tap water contamination with this element is possible. In addition, this water quality report is related to the water analysis of a month only.

Concentrations (mg L^{-1}) of the elements from K to Sr in P3 and P4 samples were below their TXRF *LQ*s. This shows the efficacy of the water purification system at CENA's plant. These results agree with conductivity measures carried out on a daily basis. The average conductivity value in P1 sample was 300 μS cm^{-1} and it ranged from 0.8 to 2.7 μS cm^{-1} in P3 sample (after anionic and cationic exchange resin percolation). pH ranged from 6.0 to 8.0 in P3.

It is possible to improve the TXRF *LQ*s through some spectrometer parameter changes such as increasing the X-ray tube voltage and current or even rising the acquisition time. For instance, if the excitation and detection time were 1000 s instead of 300 s, the *LQ* would decrease by 1.83 times. But, it is worthy to keep in mind that though the sensitivity increases at higher current and voltage, it lessens the life-time of X-ray tube. So, the analyst should assess the *pros* and *cons* of each parameter of choice. Moreover, TXRF does not need gas carrier to run the analysis as opposed to others spectrochemical techniques. As a practical example of the importance of TXRF monitoring, CENA's research laboratories can be cited. Some of them analyze macro and micronutrients in soil, plant and animal samples. In these samples, K is analyzed by flame photometry and Ca, Mn, Fe, Cu and Zn by flame absorption atomic spectrometry (FAAS) on a routine basis. For these elements, the TXRF *LQ*s is either similar to flame photometry's and FAAS's or even lower. Thus, deionized water from CENA's production plant could be directly used in analytical standard solution and sample preparations for determining the elements mentioned above when TXRF monitoring is carried out. For a better deionized water quality monitoring, it would be important to evaluate

Na, Mg, Cl and S too. However, for the determination of these elements by TXRF, it is necessary to carry out the analyses under vacuum and a thinner Be window detector is recommended.

In another example, the CENA's Stable Isotope Laboratory uses roughly 1000 L of deionized water for ammonium-^{15}N enrichment on daily basis. Although there aren't any specific critical concentrations for metal levels for these procedure, the higher metal concentration in the purified water, the lower is the life-time of enrichment column. On the other hand, though each metal has its unique interaction with cationic resin at CENA's plant, it is expected that other minor metals in tap water, such as Na and Mg, have K and Ca similar adsorption behaviors (those latter ones monitored by TXRF satisfactorily). The actual CENA's deionized water quality concerning metal levels fulfill this Laboratory needs.

Conclusions

The proposed approach turned out capable of determine Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb at concentrations higher than 40–100 µg L^{-1}, and for K, Ca, Sc, Ti, V and Sr at concentrations higher than sub mg L^{-1} in the samples during a deionized water production. Besides the low operational cost (not need gas carrier to run the analysis), TXRF has the advantage of being a multielemental and simultaneous technique. Deionized water production plant is an effective purification water system for its use for all analytical steps in K, Ca, Mn, Fe, Cu and Zn evaluation in soil, plant and animal samples as long as TXRF monitoring is taken into account.

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