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Water quality control for the Argonauta reactor in Rio de Janeiro

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ABSTRACT

Different parameters should be monitored at a nuclear facility. Among them, water used in a nuclear reactor must meet strict specifications. The research reactor Argonauta, located in Rio de Janeiro, uses light water as both moderator and coolant. Quality control is the set of measurements to ensure, at any time, products that meet the parameters and standards in force. Then, the water quality control of Argonauta encompasses physical-chemical and radiological tests that are performed periodically to monitor deviations in the water parameters specification. These tests include the measurement of pH, conductivity, and gamma spectroscopy. By means of these tests, it is possible to evaluate if the quality parameters of this water meet the requirements defined by the reactor manufacturer and the Radiation Protection standards. In this way, the safe operation of the Argonauta is guaranteed, besides avoiding unwanted exposures of operators and the environment to the ionizing radiation. This work presents the detailed assays performed in the water quality control of the Argonauta research reactor. In addition, the obtained results in 2018 measurements, and highlights of the improvements to be done are also addressed. Moreover, a comparison among other research reactors in Brazil concerning this monitoring is presented. The obtained results indicate that pH and conductivity meet the established limits of 5-6 and < 1 $\mu S \cdot cm^{-1}$, respectively. Radiological measurements indicate that the fuel element is preserved.

Keywords: **Argonauta, research reactor, water quality control.**

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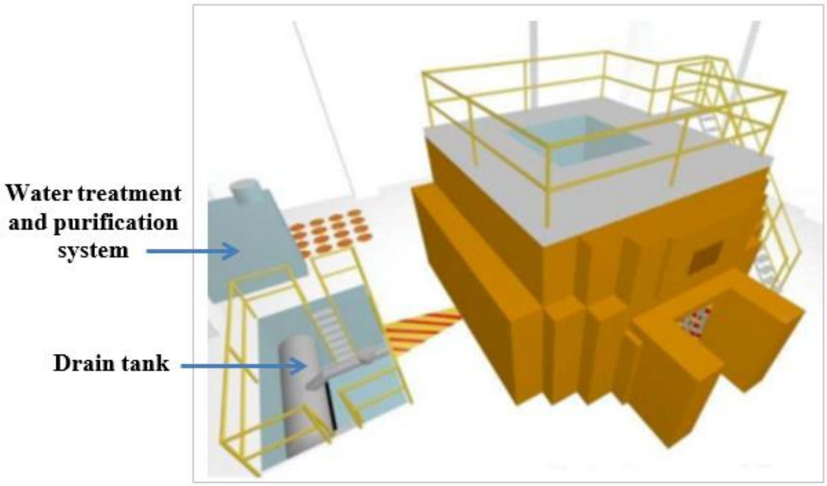
1. INTRODUCTION

A variety of parameters should be monitored in a nuclear facility. Among them, the water used in a nuclear reactor must meet strict specifications [1-3]. The Argonauta research reactor, located in Rio de Janeiro, uses light water as both a moderator and a core coolant. According to its operation and maintenance manual [4-6], the Argonauta research reactor is provided with a system of purification and treatment of water (TREU SA Machines and Equipment 1965) composed of a set of filter elements (cellulose, activated charcoal, and ion exchange resins), whose purpose is to supply the drain tank with this pure water (Fig. 1).

Figure 1: *Illustration of the Argonauta research reactor.*



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This purification system promotes the removal of electrolytes, suspended solids, colloidal silica, organic matter, and free chlorine that can stem from the surrounding environment or from the corrosion processes. For example, the water contained in the drain tank may contain impurities from the metals that make up the valves of the water circulation lines (AISI 304 stainless steel or forged brass), the ducts, the drain tank itself and the pumps (AISI 304 stainless steel) [4-6]. With this treatment, chemically pure water is obtained, thus preventing the corrosion and incrustation of ducts, equipment, the parts of the core, and, above all, of the fuel element. In addition, the absence of these substances minimizes their possible activation process during reactor operation [4-6]. The capacity of the drain tank is 1.23 m^3 and replenishment with high purity water is no more than 60 L per month. This replenishment compensates for significant evaporation losses occurring in the drain tank itself, small leakage losses in pump and valve gaskets, and in the reactor core during operation [4-6].

Constantly, the water contained in the drain tank passes through the treatment and purification system followed by pH and conductivity measurements. These parameters are strictly related to corrosive conditions therefore their values should not exceed 5.0-6.0 and 1.0 $\mu S \cdot cm^{-1}$ (25 ºC), respectively, according to the Argonauta reactor manual [4]. These values are considered appropriate to ensure the safe operation of the reactor without any compromise of metallic material coming in contact with water. If the pH and/or conductivity values outer the permitted range, the reactor operation is aborted not only to prevent serious damages in the water circulating system but also to avoid risk operational conditions [4-6].

Annually, diluted solutions of sodium hydroxide and hydrochloric acid are used to regenerate the ion exchange resins used in the purification system [4-6]. After this procedure, sodium can be measured by either X-ray Fluorescence or Flame Atomic Emission Spectrometry [7]. Also routinely, radioactivity measurements of this water are performed since in the event of compromising the integrity of fuel elements, the presence of some fission products is expected [8].

IEA-R1 and TRIGA IPR-R1 are the other Brazilian research reactors in operation where the water quality is also a concern [9,10]. Cegalla et al. report that the transport mechanisms of possible corrosion products in light water are: (1) Corrosion products of the activated structural material are dissolved in the refrigerant and deposited outside the core; (2) off-core component corrosion products are dissolved in the refrigerant and deposited on the surfaces subject to the neutron radiation field, and transported after different exposure times to off-core components; (3) Corrosion products in the refrigerant are activated in the neutron field and deposited outside the activation field [9]. Lucia *et al* highlight the importance of an analytical control program to monitor chemical species in the reactor water [10].

Deviations from threshold values may not cause immediate damage or serious consequences but indicate a problem. Possible causes for this inconvenient are the system natural wear and tear with routine use in the form of saturation of the filter elements, which can be recovered or replaced; wear of valves and fittings which must be replaced or the presence of chemical elements or compounds that must be identified by means of analytical techniques such as Nuclear Magnetic Resonance (NMR) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [10,11].

Regarding a quality assurance system, the quality control of Argonauta reactor light water is part of this system. Quality control is the set of measurements to ensure, at any time, products that meet the parameters and standards in force [2,11]. As an example, measurements should be performed by calibrated instruments and standard solutions to evaluate sample compliance with the acceptance criteria. In addition, the records shall include the results of analyses, inspections, tests, instruments performance monitoring, worksheets, as well as nonconformity treatments, such as equipment repairs and document review and updates. In this management system, the assays should provide accuracy criteria for analyses, specifications to analyze or control water purity, and actions required if specifications are exceeded [2,11]. Good water quality is essential to achieve the optimum reactor performance and to protect the operators of ionizing radiation exposure. This work presents the detailed procedure of the assays performed in the quality control for the water used in the Argonauta research reactor and the evaluation of the obtained results. In addition, the water monitoring of the other research reactors in Brazil is presented.

2. MATERIALS AND METHODS

Periodically, water samples are collected from the drain tank (Figure 1) to perform the following assays:

2.1. pH measurement

Weekly, for the pH measurements performed by the reactor operators, pH strips test (Merck) ranging from 0 to 14 were used at 25 ºC. The strip was inserted in a beaker containing 3 mL of the drain tank water and the obtained color was compared to the color standard scale. These data were registered in a controlled-access document. Also, for comparison, pH measurements were performed on Hanna HI 9321 pH meter with Gehaka 4.01 and 7.01 calibration solutions at 25 ºC. The acceptable range for pH is 5.0-6.0.

2.2. Conductivity measurement

Daily, the reactor operators perform the conductivity measurements on a Quimis Q795P equipment. Weekly, this parameter was also measured on Hanna conductivity meter, HI 2300 with conductivity cell DMC 10 (K = 1 cm) and standard calibration solution 12.89 $\mu S \cdot cm^{-1}$ at 25 ºC. The limit for conductivity is 1.0 $\mu S \cdot cm^{-1}$ at 25 ºC.

2.3. Radiological measurement

Before measurements, energy calibration was performed with standard sources of cesium 137, cobalt 60, and americium 241. Daily, an aliquot of 120 mL of water was collected and stored in a plastic vial to undergo gamma spectrometry for 24 h on a NaI(Tl) Canberra OSPREY DTB scintillation detector at 25 ºC. The obtained spectrum was treated using the Canberra Genie S504C software. Along the week, the presence of photopeaks was observed and compared to those ones highlighted on the first spectrum obtained in the same week. This procedure is based on a literature report [8].

2.4. Water quality control in the Brazilian research reactors

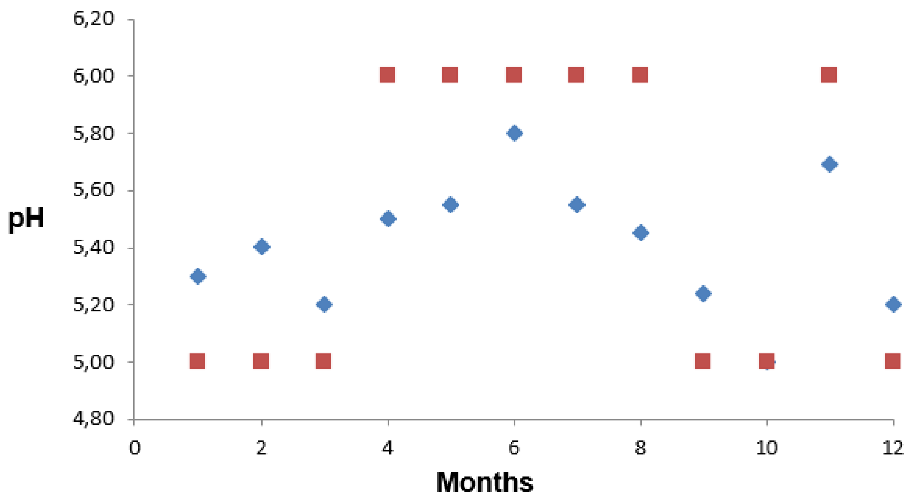
A qualitative comparison was performed considering the set of assays performed and their frequency for the research reactors Argonauta, IEA-R1, located at IPEN (São Paulo), and TRIGA IPR-R1, located at CDTN (Belo Horizonte) [9,10]. Up to date reports about nuclear reactors are not available for public access due to security issues. Nevertheless, some data regarding the monitoring program of the Brazilian research reactors found provided this comparison [9,10].

3. RESULTS AND DISCUSSION

As observed in Figure 2, pH results do not exceed the accepted range of 5.0-6.0 which is also recommended in the Argonauta reactor manual [4]. Naturally, as the pH meter is more sensitive, a bigger variation is observed in comparison with the values obtained from pH strips (Figure 2). Despite its importance, the pH parameter is not sufficient to monitor the water reactor quality. The pH changes are susceptible to hydronium or hydroxide ions released from strong acids or bases [2].

Cations from chromium and nickel elements can stem from the metallic parts of the Argonauta hydraulic system, for example. Then, a slight increase in the pH can be observed because these cations will form weak acids in the water. Besides metallic interference, pH is susceptible to the absorption of atmospheric CO_2. For these reasons, another parameter must be gathered to the pH measurement to be sure that the process is under control. In this case, electrolytic conductivity is the parameter that will signalize the corrosion of metals in the reactor hydraulic system. Standard regulations also indicate the electrical conductivity measurement of high purity water due to pH measurement susceptibilities [2]. The following comparison displays why measuring both pH and conductivity: a solution of KCl 0.01 mol·L^{-1} exhibits quite a similar pH to the ultrapure water while its conductivity is about 15 mS·cm^{-1} [13]. Due to this important alarm, the conductivity measurements are mandatory and capable of locking the reactor operation. To assure safe operations, the Argonauta reactor does not proceed if the conductivity exceeds 1.0 µS·cm^{-1} (25 ºC), which is the recommended limit reported in the Argonauta reactor manual [4].

Figure 2: *Results for the pH measurement performed by strips (in red) and by a pH meter (in blue) in 2018.*



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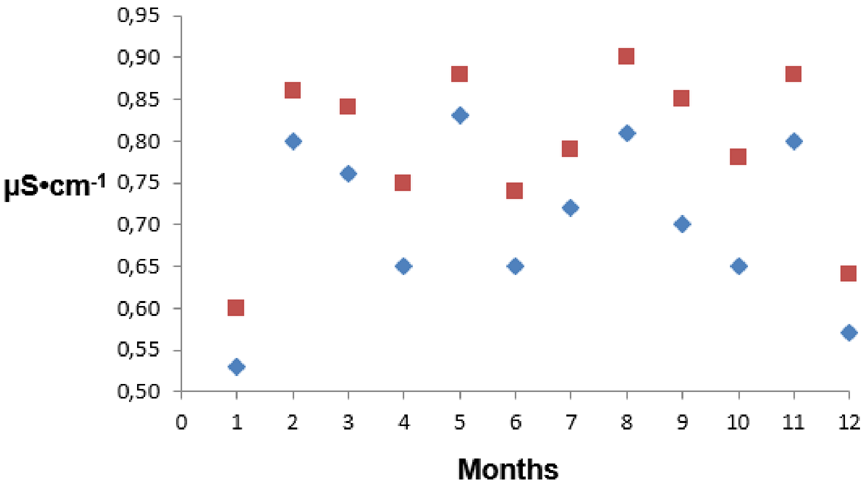
As observed in Figure 3, the results of conductivity measurements do not exceed the established limit for conductivity (1.0 µS·cm^{-1} at 25 ºC). In addition, Figure 3 shows a systematic difference between the results obtained from the equipment used. Such a difference is likely to be a result of an imperfect calibration. Both equipment were not calibrated by a certified company. In addition, the standard solution used before the measurements was not certified either. Moreover, the measurement error increases in such analysis performed in a very low range of conductivity [14,15].

Figure 3: *Results for the conductivity measurement performed by the equipment 1 (Hanna, in red) and by the equipment 2 (Quimis, in blue) in 2018.*



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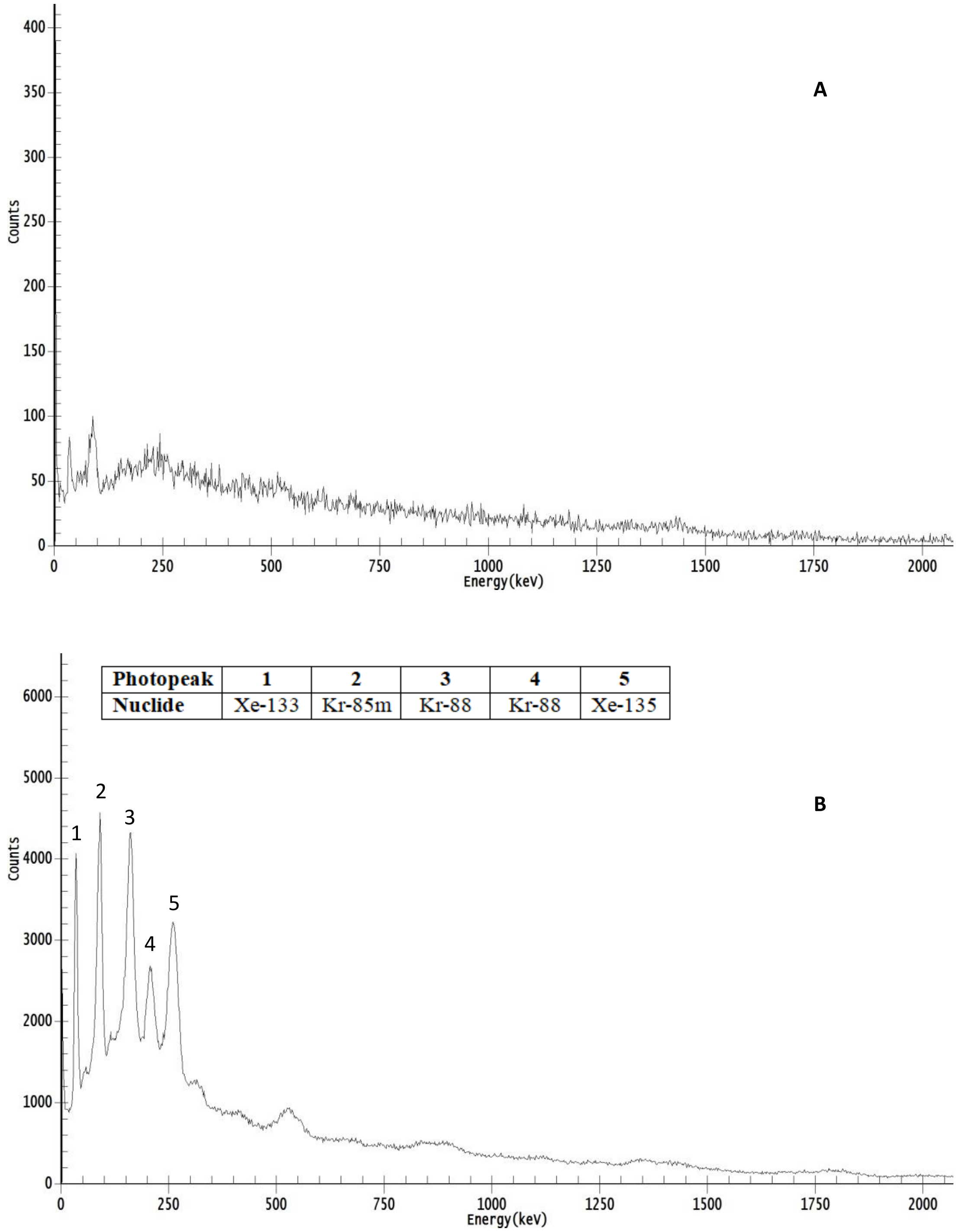
As the pH and conductivity measurements were not replicated, statistical analysis for values comparison was not performed. Nevertheless, the observed results for these parameters can indicate metallic corrosion from the aging pipelines and valves for example, or of resin saturation borderline. First, the addition of fresh purified water to the original bulk is a simple procedure to fast reduce the conductivity [2]. Secondly, resin regeneration should occur in a higher frequency. Usually, the purification system maintenance occurs at the end of the year, which explains the lowest values for pH and conductivity displayed in Figures 2 and 3 at the last and the first months [4]. Lastly, the replacement of metallic structures should be evaluated.

Recently at the Argonauta reactor, some improvements were done in the pH and conductivity measurements. A system for online measurements of pH and conductivity was installed. In a near future, comparisons among the results from this online system with a portable one will be performed to evaluate the new system performance.

Regarding results for radiological measurements, counts increased forty times after Argonauta operation (Figure 4). As no efficiency curve was used, it is not possible to quantify the arising photopeaks [16]. Moreover, potassium 40, that is usually present in gamma spectra, was not identified by means of a photopeak in the region of 1400 keV (Figure 4). This qualitative analysis indicates that the current detection system should be replaced for an HPGe detection system, for example, to provide more detailed results.

Although the fuel elements of the Argonauta reactor are coated by aluminum, the presence of noble gases in the water is observed (Figure 4). According to the literature, these noble gases correspond to xenon 133 and 135, krypton 85m, and krypton 88 [17]. These radioisotopes were also observed in an early report [8]. In the Argonauta reactor, gases escape the first protection barrier, which is formed by aluminum, through the existent micropores in it. Since the solubility of gases in water is very low and not zero, gamma spectroscopy was capable of detecting radioisotopes of Xe (xenon) and Kr (krypton) present in the water sample [18,19]. The physical half-life of these fission products is short and, therefore, does not imply the suspension of the reactor operations. Figure 4 also indicates that impurities likely to be present in the water were not activated.

Figure 4: *Obtained spectra before (A) and after (B) Argonauta operation in the following conditions: 120 min at 500 W with neutron flux exit in the J9 channel without collimation.*



Source: Authors

In Table 1, the water quality control of the reactor TRIGA IPR-R1 comprises a range of ions quantification that was signed as ‘other’. There is the quantification of ions such as aluminum, copper, lithium, manganese, zinc, mercury, ammonium, sulfate, nitrate, and nitrite [9]. Regarding pH and conductivity, these assays and their frequencies for the reactors IEA-R1 and Argonauta are quite similar (Table 1). On the other hand, chloride quantification is not yet considered for the latter [4,5]. In a near future, qualitative and quantitative studies of the possible ions present in the Argonauta moderator will be performed, as suggested by international guidelines [2]. Similarly to the TRIGA IPR-R1 research reactor, some anions like sulfate and chloride will be evaluated in the water quality control of the Argonauta reactor by using ion chromatography [10].

Table 1: Assays performed in the water quality control of research reactors in Brazil and their respective frequency.

Assay	pH	Conductivity	Chloride	Radiometric	Other
IEA-R1	•	•	•	•	-
TRIGA IPR-R1	•	•	•	•	•
ARGONAUTA	•	•	-	•	-

Assay	pH	Conductivity	Chloride	Radiometric	Other
IEA-R1	d	d	d	w	-
TRIGA IPR-R1	w	w	m	w	m
ARGONAUTA	d	d	-	d	-

d = daily w = weekly m = once to twice a month

Additionally, Table 2 displays the stated limits of pH and conductivity for the Brazilian research reactors. Naturally, the observed differences among these limits of the parameters are due to the own characteristics of each reactor. The reactor power, building features, water purification and storage, pipes and pumps, and frequency of usage or maintenance, for example, directly impact on the type and the number of impurities present in the water. According to the literature, metallic corrosion is quite reduced when pH is kept between 4.5 and 7 and conductivity is below

1 µS.cm^{-1} [2]. These limits are strictly followed in the Argonauta reactor while just the recommended pH range is used by the other Brazilian research reactors (Table 2).

Table 2: Lower (L) and upper (U) limits of pH and conductivity (µS·cm^{-1}) for the Brazilian research reactors.

Reactor	**ARGONAUTA**		**IEA-R1**		**TRIGA IPR-R1**	
Limits	L	U	L	U	L	U
pH	5.0	6.0	5.5	6.5	5.5	7.0
Conductivity	-	1.0	-	2.0	1.0	3.0

Regarding the IEA-R1 research reactor, a report shows the behavior of pH, conductivity as well as radionuclides concentration from 1995 to 1997 [9]. Without huge variations, pH was kept between 5.60-6.40 and the upper limit of conductivity was not exceeded in a so long period (Table 2). Unlike, these parameters exhibited significant variations in the water quality control of the Argonauta research reactor in just one year (Figures 2 and 3). This is an indication that improvements should be done to reach higher quality water. Since the limits of the parameters are not crossed, safe operations are guaranteed. However, variations must be decreased to avoid possible breakthroughs. Among the radionuclides presented in that IEA-R1 reactor report [9], no match was found with the identified radionuclides in the water of the Argonauta research reactor (Figure 4B). Important to mention that for the IEA-R1 research reactor this evaluation is associated with failures indication and the release of fission products, i.e., a security parameter [2,9].

From June 2011 to May 2012, pH, conductivity, and radiometric analyses were performed at the TRIGA IPR-R1 research reactor [10]. Respectively, pH and conductivity were below 7 and 2 µS·cm^{-1}, i.e., under the specified limits (Table 2). Differently from the observed in Figures 2 and 3 for the Argonauta research reactor, the variation of the results was small and homogeneous. Still in this period, gamma spectrometry indicated the presence of arsenic 76, sodium 24, and tungsten 187 in the water used in the TRIGA IPR-R1 research reactor. In addition, activities related to alpha and beta emitters were measured to evaluate faults in the fuel element and the activation of corrosion products, the presence of elements from the environment or fission products [10]. The radiometric assay performed at Argonauta is simpler. Just in case, a further radiometric investigation is performed as described on the reported procedure [8].

Due to the lack of detailed information concerning the techniques and methods used in the water quality control of the reactors IEA-R1 and TRIGA IPR-R1, a full comparison with the assays reported herein was not possible [9,10].

4. CONCLUSION

Water quality control at the Argonauta research reactor has been performed to assure its safe operation. The obtained results indicate that pH, conductivity, sodium levels, and radiological parameters meet the established limits. However, some improvements should be done. First, the use of the HPGe detector can identify and quantify both normal and suspicious peaks in the sample. Second, metals originated from the fuel element or ducts such as aluminum and chromium can be quantified applying ion chromatography technique. This technique can be also used to measure sodium levels after performing the regeneration procedure for the ion exchange resins. Finally, the implementation of a quality management system can result in more efficient and reliable procedures and registration. These improvements can increase the measurement reliability to assure a safer reactor operation and to achieve quality on a regular basis. Despite the differences among the assays performed in the water quality control for the Brazilian research reactors, the relevant assays are performed for all of them, which are pH, conductivity, and radiometric. The limits for these assays meet the current guidelines and attend each research reactor's own features.

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