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Evaluation of reuse water at the Pinheiros Subway Station in the city of São Paulo (Brazil) regarding the presence of metals using X-ray fluorescence technique with syncrotron radiation

Avaliação da água de reuso da Estação Pinheiros de metrô da cidade de São Paulo (Brasil) quanto a presença de metais pela técnica de fluorescencia de raios-X com radiação síncrotron

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ABSTRACT
Ensuring the conservation of water reserves is a challenge for all of humanity, which makes it essential to continuously study new forms of treatment and use of water sources on the planet. One of the focuses of water conservation and sustainability is the reuse of water sources in order to ensure the continuity of the main reserves of drinking water for thirsty activities and food production. This research aimed to investigate the quality of water used for reuse in the Pinheiros subway station in the city of São Paulo (Brazil) in order to evaluate the degree of presence of heavy metals and other chemical elements by the technique of X-ray fluorescence by synchrotron radiation of the Brazilian Synchrotron Light Laboratory (LNLS). The data collection for a sample collected in the summer and analyzed revealed a pH of 6.8 and the presence of 19 chemical elements by the technique with concentrations in the order of $^{ng.mL-1}$, with emphasis on the presence of lead (Pb).

Keywords: Water, Reuse, Sustainability, Water economy.

1 INTRODUCTION

The water resource is an important constituent for the existence of life. The survival of all living beings and their supply in quantity and quality is vital for the maintenance of humanity.

The reflection of the importance of drinking water sources can be noticed by the presence and development of ancient civilizations such as Egyptian, Babylonian and Greco-Roman. Since such peoples only prospered and developed thanks to nearby drinking water reserves in their territories.

According to Shiklomanov (1997) in quantitative terms, the total volume of water existing on Earth is constant and only 2.5% of this is made up of fresh water. However, of the 2.5% freshwater portion, only 0.3% constitutes the surface portion of water present in rivers and lakes, which are amenable to human exploitation and use.

Shiklomanov (1997) exposes that when analyzed in qualitative terms, water is a molecule composed of hydrogen and oxygen capable of transporting biotic and abiotic substances and molecules from the earth's surface to rivers, lakes, oceans and aquifers, making them a point of concentration of the materials carried, such a characteristic gives water the title of universal solvent.

The dizzying growth of the human population and the great upsurge of the industrial and technological sector has led to an increasingly accelerated and massive demand for sources of clean water for public supply and as raw material for the primary and secondary sector.

Because the surface reserves are constant and the great environmental impact generated by the misuse of water sources, which causes major environmental disasters with rampant pollution of water bodies, makes it important to study technologies and methodologies that aim to preserve potable sources and consequently preserve life on the planet.

According to projections of the United Nations (UN) indicate that, if the trend of consumption and pollution persists, by 2050 more than 45% of the world population will be living in countries that will not be able to guarantee the minimum daily quota of 50 liters of water per person (MELO JÚNIOR *et al.*, 2019).

2 OBJECTIVE

The purpose of the research was to evaluate the relationship of heavy metals and other chemical elements present in the reuse water, coming from the rainwater source, captured and stored in a well for use in general activities at the Pinheiros subway station in the city of São Paulo, Brazil. Remembering that the use employed on site is varied with the exception of potability.
For such a study, the technology of high standard by synchrotron radiation was used thanks to the support of the Brazilian Synchrotron Light Laboratory (LNLS).

3 LITERATURE REVIEW

3.1 WATER RESOURCES IN BRAZIL

According to Lima (1999) due to the territorial dimension of Brazil, it presents great variations related to climate, geology, relief, vegetation and also water resources, economic and social development and population distribution.

Based on the distribution of surface waters, the Brazilian territory holds 13.7% of the fresh water of the globe. Emphasizing that the surface reserves of fresh water on the planet are only 0.3% (MARTINS, 2003).

Most of the Brazilian reserves of surface fresh water are found 73% (of the 13.7% in global reserve) in the northern region of the Amazon basin, which is inhabited by less than 5% of the Brazilian population (LIMA, 1999).

On the other hand, only 27% of Brazil's surface water resources are available to other regions, where 95% of the country's population resides (LIMA, 1999).

Poor water distribution causes problems to possible supply crises in the centers of greater demand, and the problems are greater in watersheds where water withdrawals exceed water availability, which forces the search for alternative sources of water by the population. In this context, the basins near large urban centers are the most affected, in addition to having the aggravating factor of compromising water quality due to uncontrolled urbanization, which causes an increase in treatment costs and restricts water uses (ANA, 2005).

In rural areas, the main interferences to water resources are due to the destruction of permanent vegetation areas, the indiscriminate use of pesticides and fertilizers and the poor disposal of animal and human waste. All these contaminants are carried by the water with the soil particles or are deposited directly in the surface water sources (GONÇALVES, 2003).

According to Gonçalves (2003) one of the great limiters of crop productivity is the supply of water. Thus, the use of technologies aimed at irrigating crops increases more and more and with it comes a greater consumption of water, an increase in the number of dams, reservoirs, exploitation of rivers and even groundwater. In addition, in agriculture the waste of water is very large, especially in the irrigation of crops, when using systems by furrows or by flooding. In this way, in quantitative terms, agriculture becomes the major user of water resources.

According to Shiklomanov (1997) on average, the agricultural sector uses 70% of the total fresh water consumed, followed by the industrial sector (20%) and the water destined for supply (10%).

Concomitantly, the acquisition of inputs such as fertilizers and pesticides has increased significantly, which are considered essential products to obtain high productivity ceilings. However, the massive use of these inputs can have serious consequences for the environment and for man himself, and may cause contamination of both terrestrial and aquatic resources (LIMA, 1999).

Thus, according to Von Sperling (2000) agriculture has become a major source of diffuse pollution of surface water, due to the use of soil without respecting its capacity to support and simplify production, through the adoption of technological packages.

3.2 ADVANCES IN ENVIRONMENTAL LEGISLATION

In Brazil, in 1930, the Head of the Provisional Government of the Republic of the United States of Brazil, using the attributions conferred on him by the 1st of Decree No. 19,398, of 11/11/1930, and, on July 10, 1943, through Decree No. 24,643 establishes the Water Code. Among the formulations of the legislation, there is the Treaty on Environmental Education for Sustainable Societies and Global Responsibility, presenting 16 principles, among which stands out principle 16, described below: Principle 16 - Environmental education should help develop an ethical awareness about all the forms of life with which we share this planet, respect their life cycles and impose limits on the exploitation of these forms of life by human beings. By signing this Treaty, the organizations proposed to program twenty-two essential guidelines, and agreed, among other things, to disseminate and promote in all countries the Treaty on Environmental Education for Sustainable Societies and Global Responsibility through individual and collective campaigns, promoted by NGOs, social movements and others (MARTINS, 2003).

In Brazil, Law No. 9,433/97, known as the Water Law, turns 22 years old in 2019 and has brought advances in the field of management of national water resources, such as the elaboration of the National Water Resources Plan (PNRH), approved in 2006 (MARTINS, 2003).

3.3 WATER REUSE

As reported by Cetesb (2023), the reuse or reuse of water or the use of wastewater is not a new concept and has been practiced around the world for many years. There are reports of its practice in Ancient Greece, with the disposal of sewage and its use in irrigation. However, the growing demand for water has made the planned reuse of water a current and important topic.

In this sense, water reuse should be considered as part of a broader activity that is the rational or efficient use of water, which also includes the control of losses and waste, and the minimization of effluent production and water consumption (CETESB, 2023). Within this perspective, treated sewage plays a fundamental role in the planning and sustainable management of water resources as a substitute for the use of water intended for agricultural and irrigation purposes, among others.

3.3.1 Types of Reuse

According to CETESB itself (2023) the reuse of water can be direct or indirect, resulting from actions planned or not by the responsible sector. It is important to differentiate each type of reuse water.

3.3.1.1 Unplanned indirect reuse of water

This process occurs when water, used in some human activity, is discharged into the environment and again used downstream, in its diluted form, in an unintentional and uncontrolled manner. Walking to the point of capture for the new user, it is subject to the natural actions of the hydrological cycle (dilution, self-purification).

3.3.1.2 Planned indirect water reuse

This type of reuse occurs when the effluents, after being treated, are discharged in a planned way into surface or groundwater bodies, to be used downstream, in a controlled manner, in the attendance of some beneficial use. The planned indirect reuse of water presupposes that there is also a control over the eventual new discharges of effluents on the way, thus ensuring that the treated effluent will be subject only to mixtures with other effluents that also meet the quality requirement of the targeted reuse (CETESB, 2023).

3.3.1.3 Planned direct reuse of water

In this type of reuse its use process occurs when the effluents, after being treated, are sent directly from their discharge point to the place of reuse, not being discharged into the environment. It is the case with the highest occurrence, intended for use in industry or irrigation (CETESB, 2023).

3.4 X-RAY FLUORESCENCE

Kneip and Laurer (1972) describe the advantages of X-ray fluorescence by energy dispersion over wavelength scattering. Initially, the quantitative analysis with XRF required many standards, for the construction of calibration curves of the system or for calculations of the so-called alpha coefficients.

Alpha coefficients are constant correction factors and at least **n-1** standards are required; where **n** is the number of elements present in the sample (KNEIP and LAURER, 1972)

This method is based on corrections that are performed due to the interferences produced by an **element i1** in the intensity of the fluorescent radiation of an **element i2** present in the sample.

Another method, using the physical principles of X-ray fluorescence production, was developed by Criss and Birks (1968). It is known as the Fundamental Parameters Method, this method is based on the analytical solution of theoretical equations that describe the dependence of fluorescent radiation intensity in terms of fundamental physical parameters and instrumental parameters. The method is simple and does not require a large number of standards, making it currently one of the most widely used and widespread methods in terms of XRF.

3.4.1 Total reflection synchrotron radiation fluorescence (TXRF)

Yap *et al.* (1989), used X-ray fluorescence by total reflection for the analysis of fine samples of mineral sand.

The total reflection X-ray fluorescence method was tested with certified rock samples (JB-3J). They evaluated that the method has some advantages, being: multi-elementary; with simplified sample preparation; contribution of low scattered radiation and need for small amounts of digested samples, about 2 ml, for analysis.

Chen *et al.* (1990), showed that the sources of synchrotron radiation have important characteristics for the analysis of materials, mainly by the ability to determine the elemental composition and molecular structure. They reported that for microscopic analysis (micro characterization of materials), synchrotron radiation sources offer a spatial resolution of 10 μm with a detection limit between 10 and 100 ppb.

Salvador (2003) used a total reflection X-ray fluorescence system (TXRF) to analyze samples of mineral and vegetable oils, using different sample preparation techniques. The direct preparation of dilute oil solutions showed good results for the concentrations of elements at trace levels higher than 1 μg.g-1.

Liendo *et al.* (1999), described a comparative study between PIXE and TXRF for the analysis of Cl, K, Ca, Fe, Cu, Zn and Br in human amniotic fluid. They found agreement in the measurements performed with the two techniques for the following elements: K (100%), Cl (60%), Fe (80%), Cu (50%) and Zn (50%). They reported the need for further studies in order to establish

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the ideal experimental conditions that lead to a complete agreement between the TXRF and the PIXE.

4 METHODOLOGY

4.1 CASE STUDY

The research was based on analyzing the reuse water of the Pinheiros subway station located in the city of São Paulo, Brazil.

Figure 1 shows a view of the station's location.

Figure 1: Overview of the Pinheiros subway station.

The region comprised by Figure 1 (above) has as a fundamental characteristic that it is a region of great importance and mass circulation of people. The Pinheiros station has an average flow of 60 thousand passengers per day. It is also an important transportation exchanger, with access to the Metro and the Companhia Paulista de Transporte Metropolitano (CPTM).

Line 4 (see figure 1) which corresponds to the study line, called the yellow line, has about 13 km of route with 11 stations allocated along the route.

The station has the process of capturing the local rainwater network in order to use rainwater for general activities within its installation, that is, the use of a rainwater reuse system in order to minimize costs and allow a process of local sustainability.

Thus, the research aimed to verify the quality of the water in relation to the levels of heavy metals and other chemical elements present by the synchrotron radiation technique.

An aliquot of 500 mL of reuse water from the locality of study interest was taken for analysis in scientific research. The sample was collected in the Brazilian summer and frozen for its multielemental analysis and acidity/alkalinity degree.

4.2 SYNCHROTRON RADIATION ANALYSIS BY TOTAL REFLECTION

The research project included the analysis of the chemical elemental concentration present in a sample of reused water from rainfall in the locality of study interest (figure 1).

The aliquot sample collected was 500 mL, and it was previously frozen at -5^{0C} for conservation of its initial characteristics.

The technique for analysis adopted was carried out at the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas by the process of total reflection with the use of synchrotron radiation that allows a multielemental analysis of the chemical compounds present in bottled rainwater without the need for destruction of the samples by acid action. Such a process allows a clearer and concise analysis of the concentration and a wider spectral range of analysis by the adopted radiation beam.

4.2.1 Synchrotron Radiation with Full Reflection metal detection tool

In the analysis by total reflection, an aliquot of 1 mL of reuse water (from the 500 mL bottled) of the study was removed and a Gallium standard of 100 μL (102.5 mg) was added with the use of an automatic pipette. L-1) used as the internal standard, resulting in a concentration of 9.32 mg. $^{L-1}$ of the standard in the sample.

The internal standard was used to eliminate the non-uniformity of the aliquot in the support, because the thin film formed on the substrate does not have regular geometry. Thus, the intensity of the X-rays obtained in the irradiation of the sample depends on the position in which it was placed on the support, as reported by Melo Júnior (2007). With the addition of the internal standard, the result obtained will always be in relation to this standard, not mattering, in this way, the position of the sample (MELO JÚNIOR, 2007).

At the end of the preparation, 5.0 μL of the resulting solution was then pipetted under a lucite plate and the sample was dried with the aid of an infrared lamp, as shown in Figure 2.

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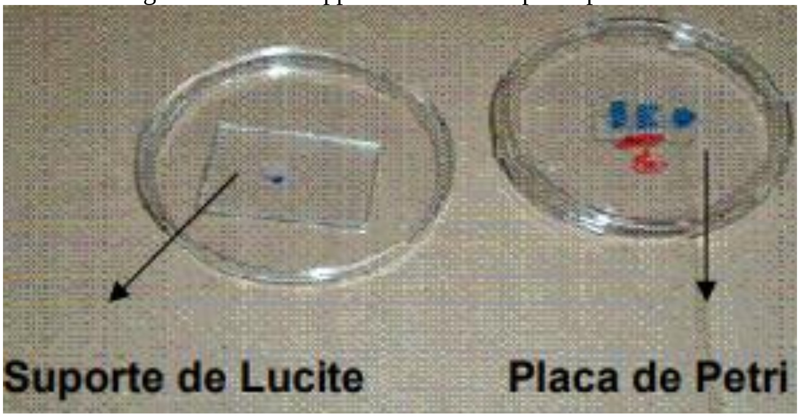
Figure 2: Lucite support used for sample deposition.



4.2.2 Installations of the Synchrotron Radiation Line – Total Reflection Technique

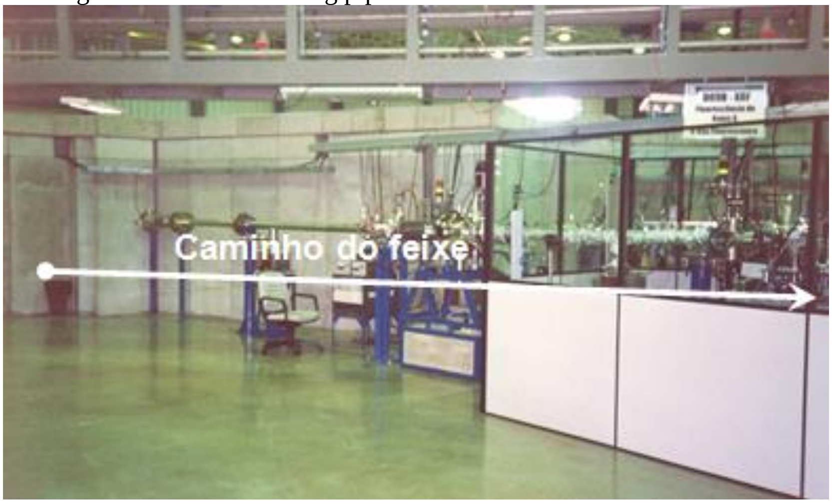
The synchrotron radiation line for total reflection is intended for the analysis of the multielemental chemical composition (Z ≥ 13) in scientific applications of trace element determination in environmental, biological and materials sciences, chemical depth profile of thin films and chemical mapping. It operates with a beam from 4 to 23 KeV, in table 1 there are other characteristics of the line (MELO JÚNIOR, 2007).

Table 1 - General Characteristics. Source: Brazilian Synchrotron Light Laboratory. www.lnls.br (2023).

Source	Deflector magnet D09B(15º), σy = 0.222 mm, flow in sample: 4 x 109 photons/s at 8 keV.
Monochromator	Monochromator *channel-cut.*
Crystals	Si (111) (2d=6,217 Aº): 4-14 keV (E/ΔE=2800); Si (220) (2d=3.84 Aº): 5-23 keV (E/ΔE=15000).
Detectors	Hyperpure Ge (150 eV resolution) and Si(Li) (165 eV resolution) solid-state detectors; photodiodes and ionization cameras.
Optics	Capillary optics with 20 µm spatial resolution.
Sample handling	Vacuum chamber (2-10 mbar) with conventional excitation geometry (45º - 45º). Stations for experiments the grazing incidence and 2D mapping, both with total control of sample positioning.

Figure 3 shows the pipe of the DO9B – XRF line, used in the experiment, through which the synchrotron light beam of the ring passes to the fluorescence experimental station located at LNLS.

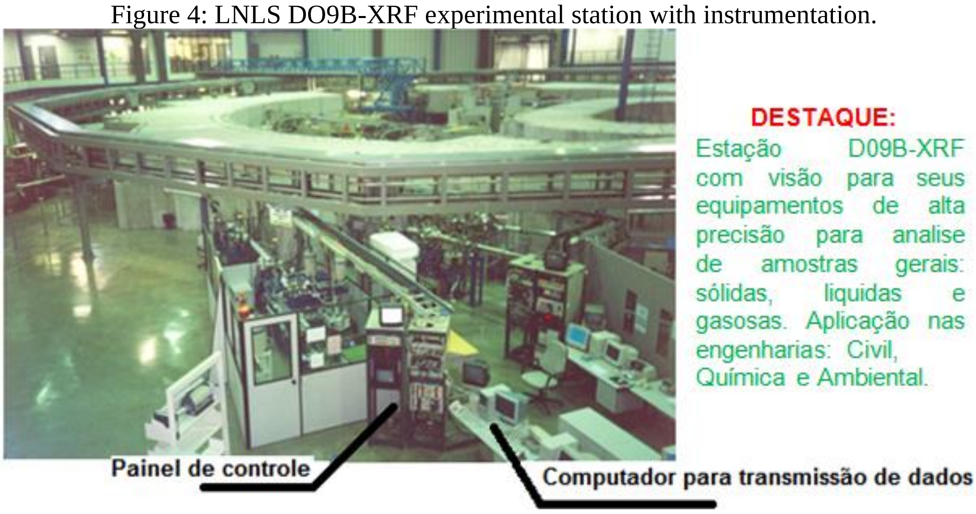
Figure 3: Photo of the ring pipe for the DO9B – XRF line of LNLS.



In the experimental station of X-ray fluorescence (figure 3), for the detection of X-rays a hyperpure semiconductor Ge detector was used, with a beryllium window of 8 μm thick, an active area of 30 mm2, coupled to an amplifier module and with a multichannel analyzer plate, inserted in a microcomputer.

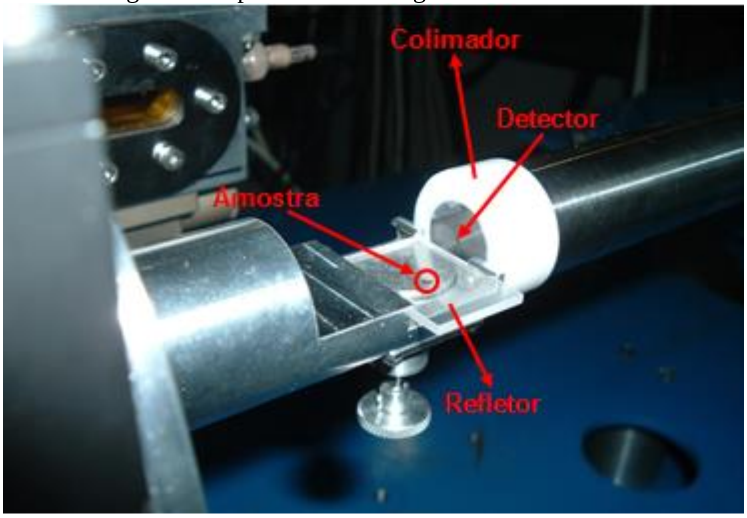
Figure 4 shows station D09B-XRF and a partial view of the radiation ring.

Figure 4: LNLS DO9B-XRF experimental station with instrumentation.



The experimental arrangement allows the rotation and translation of the sample in order to obtain the condition for the total reflection of the incident beam on the sample that is allocated in the rectangular plate of lucite (*Perspex) fixed in the sample* holder, allowing the measurement of the chemical elements contained in the sample. Figure 5 shows in detail the sample of rainwater (reuse) deposited on the reflector and the detector with the collimator. It is important to highlight that for statistical purposes triplicates of the same sample were made for a better accuracy of the data captured by the technique.

Figure 5: Experimental arrangement of SR-TXRF.



4.3 PH ANALYSIS

Care was taken to analyze the degree of acidity/alkalinity of the sample that was the focus of the research.

For this purpose, a conventional pH meter was used, and the PH-127 Digital model from Conteck was adopted.

This meter has wide use in swimming pools and for its practicality and low cost was chosen for use in Unicamp's partner laboratories with LNLS.

5 RESULTS

5.1 MULTI-ELEMENT ANALYSIS

5.1.1 Analysis by the Synchrotron Radiation Technique – Validation

To ensure that the detected values are reliable, a characteristic curve with defined patterns was constructed. Thus, a degree of reliability was obtained and then the collected samples were evaluated.

Elemental sensitivity was calculated using five standard solutions with known elements and at different concentrations, plus the element gallium (Ga) used as the internal standard. For this, the range for this pattern curve is called the K series.

The determined values of the experimental sensitivity for the elements contained in the solutions and the results obtained are presented in table 2, below.

Table 2 - Experimental sensitivity for the K series.

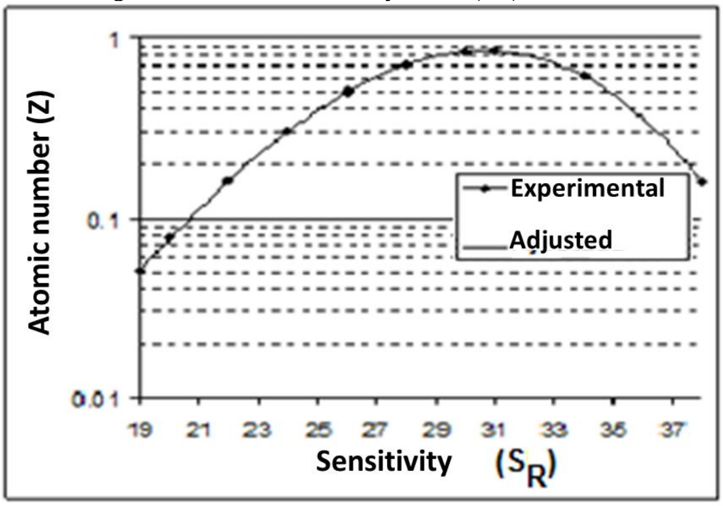
Atomic number	Chemical element	Sensitivity
19	K	0,083270
20	Ca	0,086387
22	Ti	0,199891
24	Cr	0,393820
26	Fe	0,593576
28	Ni	0,796228
30	Zn	0,897568
31	Ga	0,975819
34	Se	0,809614
38	Sr	0,306673

5.1.2 Reliability curve

By using the data obtained from table 2, the reliability degree curve was raised from a characteristic graphic curve, called the relative sensitivity curve for series K. Figure 6 (below) shows the reliability characteristic curve for the elements in the range of study interest.

Such a curve is important to align the error deviation and reflect on the accuracy of the analyses and ensuring a reliability of the data analyzed.

Figure 6: Relative sensitivity curve (S_{Ri}) for K series.



The sensitivity curve shown in Figure 6 initially allowed the use of certified samples with known values. This made it possible that by using the same energy beam in the sensitivity curve for the certified samples, the values were close to the pre-defined ones, thus allowing the samples collected and analyzed to have their values really within reality without detection errors.

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5.1.3 Pattern Tuning by NIST

The adjustment was made with a standard certified by the *National Institute of Standards and Technology* (NIST).

Tabela 3 have the samples certified by NIST to the standard called by NIST as *Drinking Water Pollutants,* with the values measured in the LNLS and those certified by NIST, respectively.

Table 3 - Comparison of values measured in LNLS and certified by NIST.

Element	Measured Value and Confidence Interval (mg. L-1)	Certified Value and Confidence Interval (mg. L-1)
Cr	8.91 ± 0.18	8.89 ± 0.45
As	8.66 ± 0.17	8.77 ± 0.45
Se	4.87 ± 0.07	4.69 ± 0.23
Cd	4.55 ± 0.64	4.54 ± 0.23
Ba	89.99 ± 0.76	91.89 ± 4.55
Pb	10.03 ± 1.01	10.09 ± 0.45

5.1.4 Results from the rainfall sample

Only after this validation of the system was then that the sample of dry rainwater in the lucite plate was used, in which table 4 can evaluate the average concentrations of the chemical elements measured.

Table 4 - Mean concentration (ng.mL-1) of the elements present in the rainfall sample.

Chemical Element Symbol	Concentration ng.mL-1
Al	126,40
S	140,00
Cl	372,70
K	16,80
Ca	738,50
Ti	1,60
Cr	19,60
Mn	13,00
Fe	118,50
Co	0,60
Ni	0,80
Cu	29,95
Zn	679,60
As	2,20
Se	0,70
Br	1,30
Sr	2,32
Hg	10,50
Pb	35,90

The values found of the elements in table 4 make it possible to verify the degree of water quality. It can be noted that the presence of lead concentrations (Pb), chromium (Cr) and mercury (Hg) among the others reflects the locality of study that has a high level of motor vehicles of combustion of hydrocarbons that emit these compounds in the air, being "washed" from the local air by the rain and stored in the water of reuse.

5.2 PH ANALYSIS

Thanks to the use of the pH meter model PH-127 Digital from Conteck. It was possible to measure the average pH value of the rainwater collected, which revealed an average pH of 6.8. This showed a slight acidity of the rainwater studied in question.

The values found in table 4 (previous), as well as pH presented a value of water quality of reuse acceptable for general activities that do not involve: a human thirst, bathing or use in horticultural foods; since there is no data on the presence and concentration, for example, of fecal coliforms from rainwater, which is stored in a rainwater containment tank at the Pinheiros station.

It should also be considered that the sample was a punctual collection, which does not reflect the quality of the water over a greater temporal amplitude.

6 CONCLUSION

The research had an important focus for spreading more the use of an accurate and high-tech technique employed in the scientific field. However, the fact of using only one rainwater collection cannot be generalized and ensure that the water quality is the same during the year.

As implicative is the fact of the need for collections on more days of the week, as well as during the climatic seasons, especially for the summer and winter that occurs the lowest distribution of rain and consequently a greater accumulation in the levels of contaminants in the winter period in dissonance to the Brazilian summer. This implication occurs in the high concentrations of compounds from automotive combustion in the atmosphere, especially in winter.

If there were collections in this period of winter it would be very interesting to verify the dissolved levels in the reuse water at the time of "washing" the elements dispersed in the atmosphere.

But the research had the merit of the concern in researching and studying the quality of a reuse water that has great importance, showing a significant evolution in the environmental concern of the São Paulo government sector and a clear evolution of the goals of the United Nations (UN) for 2050 about water preservation.

Another fact that can be raised is the continuous need to change the energy matrix, especially the terrestrial network represented by the vehicular sector, with the adoption of new practices that minimize the automotive concentration in regions such as the one studied, which reflects the presence of toxic and harmful chemical elements to humans, especially the lead (Pb) and mercury (Hg) detected.

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