Design of a Microfluidic System for Preconditioning of Samples of Environmental Fluid or Water

Jhonatan Ribeiro
Technology College
UFAM
Manaus, Brazil
Jhonatant90@gmail.com

Valtemar F. Cardoso
Instituto SENAI de Inovação
ISI Microeletrônica
Manaus, Brazil
valtemar.cardoso@am.senai.br

Carlos R. P. dos Santos Junior
Instituto SENAI de Inovação
ISI Microeletrônica
Manaus, Brazil
carlos.pereira@am.senai.br

Marcus Vinicius Pelegrini
Instituto SENAI de Inovação
ISI Microeletrônica
Manaus, Brazil
marcus.pelegrini@am.senai.br

Abstract—Biological and chemical analysis of environmental fluids need to be preconditioned, in order to obtain a total concentration measurement of the element chosen. The water is one of the most important fluids to be analyzed and the presence of the contaminants need to be warned to allow preventive actions. A continuous flow measure can be a solution for this problem and a Sequential Injection Analysis (SIA) capable to follow all the steps in the precondition process is a challenge that need to be included in the continuous flow measurement. In this paper, the microfluidic device developed is a small reaction thermal chamber with microchannels for sample and reagents admission allowing the total element concentration in water quality monitoring. The device can improve the preconditioning process decreasing the reaction time and the volume of sample and reagents during oxidative digestion. A detailed electronic circuits and hydraulic parts applied are showed even as your functional diagram.

Keywords — Sequential Injection Analysis (SIA), microfluidics, preconditioning system

I. INTRODUCTION

Chemical analysis optimization is a crucial point to keep the water quality safety for human consumption allowing the monitoring pollutants levels in the wastewater dump points and drinking water stations. The chemical analysis system needs to have real time response and achieve the process steps autonomous using concepts like LoC (Lab-on-Chip) and µTAS (Micro Total Analysis System). Standard Methods define the main chemical analysis procedures and the processes wherein defines the volumes and reagents used in accordance with governmental criterion or agency in charge. The use of microfluidic systems allows reducing reagent consumption, shortening the analysis time and enabling an autonomous system [1].

Before any chemical analysis, it is necessary a preconditioning step in order to obtain the total concentration element required in the sample. The separation process of the target to be analyzed is called preconditioning [2]. Several analyzes with fluids are performed, so the preconditioning variety is associated with this. The action of removing other particles and concentrating the amount of target components in the analysis makes the detection methods more accurate. In microfluidics, preconditioning can be done with small amounts of samples and reagents, in addition, the process also needs to be heated and by its reduction in volume, the heating time can become much smaller, since the heat is conducted to lower volumes. With the process been done autonomously, it allows a time use in other processes.

This paper presents a design of a microfluidic oxidative digester for preconditioning liquid samples for environmental analysis. The preconditioner uses microfluidic principles for the transport of liquids and perform the process of oxidative digestion for chemical samples, capable to be adjusted according to the methodology allowing the several chemical elements analysis. In other words, the design of the device performs the preconditioning with low volumes of reagents, autonomously and delivers the digested sample for next analysis steps or conditioning it in a reservoir for analysis in a proper moment.

II. MOTIVATION

Water is a very important fluid for human life. The ingestion of drinking water in the body guarantees several health benefits. Therefore, the constantly water quality analysis with the aim to keep the human health is too important. The water analysis always follows a rigorous standard method that requires many steps to evaluate each element of interest. In the water analysis the elements need to be characterized according to your concentration and the procedure is indicated in the standard methods defining if the water is proper for drinking. The usual monitoring process take a long time and need to be carried out in laboratories, but with the benefit of automation and microfluidics systems, it can be performed automatically and with small sample volumes, thus having a more precise monitoring over the time increasing the reliability of water treatment station and warning wastewater dump criminals. The use of microfluidic autonomous systems for elements concentration analysis, especially in water, is justified due to its importance in human survival. Several works in the field of microfluidics have been performed, such as [3]. The interest element concentration analysis of the sample can be achieved in the µTAS, however when the total concentration is required the sample needs to be preconditioning and this procedure is still performed in the laboratories by technicians, without the aid of automation and microfluidics. Therefore, based on these data, this paper proposes a miniaturized and automate system to achieve these steps in the water quality monitoring autonomously.

III. MICROFLUIDICS SYSTEMS

The microfluidic systems has a behave to the fluidic dynamics in the micrometric scale and the channels need to be developed considering the flow in this scale [4]. In the microfluidic analysis systems each reaction involves reagents, samples and residues and the small volume consumption is one of the great advantages allowing an environmental friendly and economic autonomous monitoring.

The fluid flow on microscale must be precise in order to attain this necessity the piezoelectric micro pumps have been applied allowing to work with flows in order of 100µL/s [5]. The slow volumes pumping allows the reactions occur in order of µL/g.

In general, microfluidic systems are designed following the hydrodynamics laws, the fluid has in your composition an expressive number of molecules and even the concentration elements analysis can be evaluated without problem in microfluidic systems [6]. Mathematically, a point is separated from the fluid and the problem is analyzed from that point, however, physically the fluid is analyzed together and studied from its flow behaving. Usually in this scale the fluid has a laminar flow behaving which needs a difference in pressure for its movement.

With the use of an actuator, the pressure is controlled by directing the fluid flow through the microtube or flat wall channel and the reaction can be controlled by volume, by flow or even by an internal sensor ensuring reduced volumes compared with the conventional laboratory procedure.

IV. Sample Preconditioning

When we need to know a total concentration of the elements in the chemical analysis, we must free the organic compound. Therefore, the samples need to undergo to an oxidative digestion process. The presence of organic and inorganic materials in the sample, compromises the result of any chemical analysis [7]. Preconditioning can be done in acidic or basic medium over thermal influence, where the temperature stability is a paramount during preconditioning. A suitable preconditioner is adaptable to both methods, samples and reagents inputs and a suitable heater system. The oxidative digestion process converts both organic and inorganic forms of the interest element allowing the organic concentration be calculated with the difference between total chemical element measured and inorganic chemical element measured. The solution, a mix of reagents and sample, in a static chamber is heated for a standard time for the reaction. The sample preconditioned is delivered to a container or follow to a pH adjusting system for the element concentration analysis by a colorimetric device. The miniaturization of this system directly influences the volume of reagents and the heating time in the course of the process.

The system having thermal stability and precise volume control ensures that the reaction can be done under constant conditions, always with the same reaction parameters.

The preconditioning, in Fig. 1, begins with the pumping of the sample that pass through a pre-filter and 0.45um membrane filter to control particles sizes in the reaction chamber of the microfluidic device. After sample, occur the admission of the reagents in the reaction chamber and the thermal system starts to heating. The actuator responsible for the sample pumping into the chamber consists of a piezoelectric micropump. This pump creates differences in internal pressures by moving the fluid at a certain frequency. The filtration step eliminates solid impurities of the sample, present in aquatic environments, when the measure is done direct in rivers or lakes. A bi-directional valve controls the process of sample pumping, which alternates between sample inlet and cleaning solution inlet. The cleaning solution is responsible for the preconditioning rotation, in other words, it cleans the preconditioner after each process, ensuring it is ready for more samples. The sample and reagents volume in the reaction chamber are strictly stoichiometry proportional to the volumes for the preconditioning done in the laboratory but in this case without human errors, in other words more safe procedure.

The pumping sequence and volume control obey the standard method. After the reaction chamber attain the proper volume, the heating process starts in order to achieve the oxidative digestion temperature. The heating is done by a Peltier pellet, which generates a thermal difference in its faces, when subjected to a voltage potential difference. Depending on the digestion method, the time can be differentiated. After the reaction process period, a bidirectional valve B selects a certain volume for analysis and discards the excess volume and the microfluidic oxidative digester starts its self-cleaning. The cleaning solution is discarded after the cleaning process.

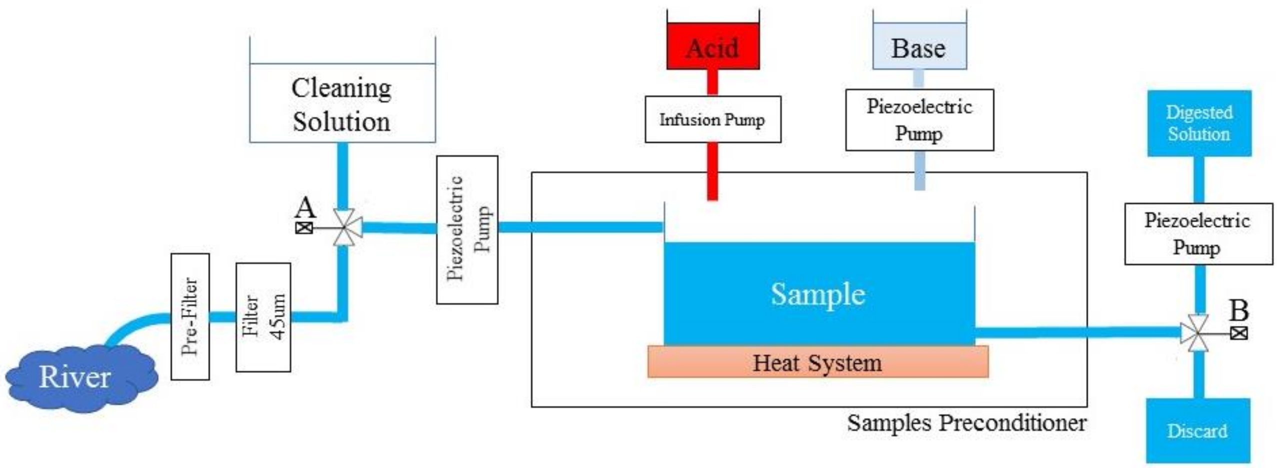

Fig. 1. Schematics of the Precondition System using the Piezoelectric Pump

V. MICROFLUIDCS SYSTEM DESIGN

The selection of the materials to develop the microfluidic oxidative digester needs to be acid resistant and capable to avoid contamination during the reaction. In the total chemical element analysis, the oxidative digestion process uses some strong acids. In the literature there is some studies that indicate several materials resistant to acid conditions and high temperatures [7]. However, besides these characteristics, the material must be manufacturable in tools such as milling cutters or laser cutting machines. Among all the existing materials, some have high hardness, which would make difficult the process of manufacture of the channels and the reaction chamber. An interesting material is the Low Temperature Co-Fired Ceramic (LTCC), that has been widely used in Micro-Electro-Mechanical Systems (MEMS) and Micro Opto Electromechanical systems (MOEMS) based on microfluidic systems [8]. Some articles highlight the versatility of the LTCC as an alternative to building microfluidic devices for continuous analysis, miniaturizing laboratories. The work highlights the ease of integration between systems with fluidic, mechanical and electronic components [9]. The versatility of the LTCC allow to develop tridimensional structures through cutting and assembly according to a positive factor for its use. In the green state, the LTCC is malleable, like a paper sheet and can be acquired commercially in square sheets of eight inches [10].

The model may analyzed in the three-dimensional shape using a software that allows such application before the fabrication. In this paper the model was evaluated by the Autodesk Inventor. This software allows you to create parts in three dimensions for analysis of fluid dynamics, heat transfer and device configuration [11].

The precondition design, provides one input to insert the sample, two inputs for insert the reagents. Also provides one output though which the sample after reaction will be directioned, with the aid of the valve, to the next step. In the next step the sample can be analyzed or discarded. In order to control the temperature during the reaction of oxidative digestion, it will be used a type K thermocouple, positioned internally. The Fig. 2 shows the schematic drawing of the microfluidic oxidative digester obtained from Autodesk Inventor 2019. Internally, the pre-concentrator has a reaction chamber, in contact with the heating device, where the reaction will occur.

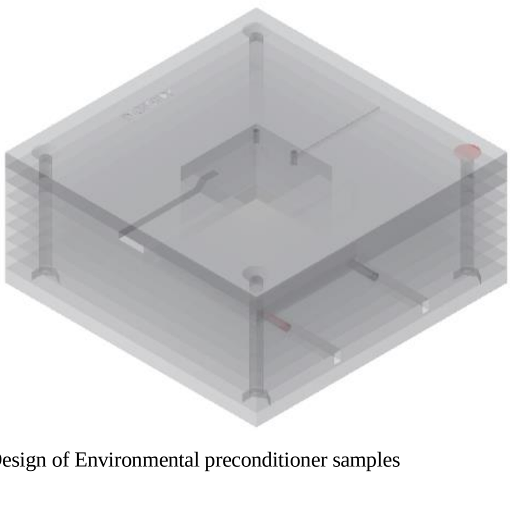

Fig. 2. Design of Environmental preconditioner samples

Considering that each LTCC sheet has 250µm thickness, in the manufacturing process to obtain a square section for reaction chamber with 30mm resulting in a volume of 5cm^3, it will be needed 23 sheets of LTCC are required. The channels are also composed of a LTCC layer sequence and have a circular cross-section of 1.9 mm^2. The bottom face of the reaction chamber is ceramic, but in direct contact with the heating device, in this case a Peltier pellet. The ceramic material ensures, according to [7], that there will be no sample contamination during the reaction process. With these measurements, the device uses small volumes of reagents and sample compared to other studies as [12].

For the manufacturing process, a CNC machine receive a tridimensional file that define through a code construction the milling path and a sequence of tools to be used. In the Fig. 3 is show the two-dimensional layers designed for the CNC fabrication.

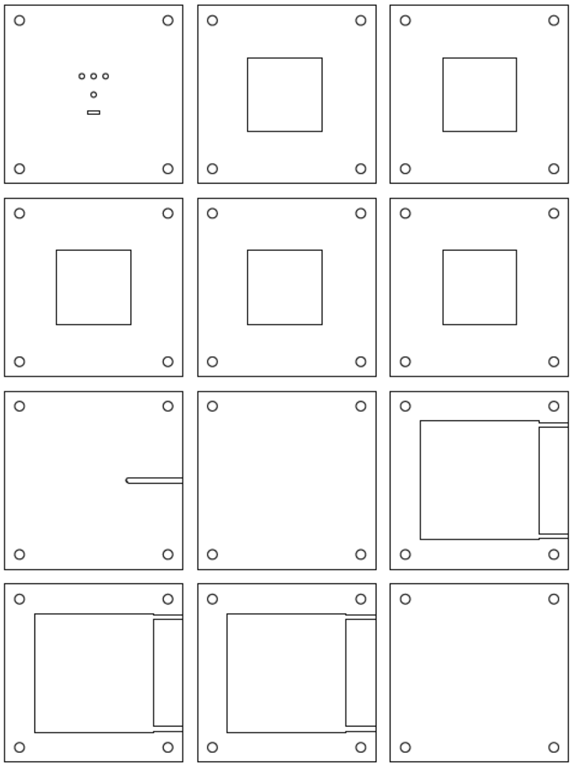

Fig. 3. Precondition faces in two dimensions

The device must ensure thermal stability and using a Peltier pellet to heat the sample it can reach up to 120°C. Studies and tests were done in order to select the most appropriate Peltier pellet, adopting initially low temperatures (between 50 and 60°C). The results of the stability tests of the controllers designed to keep the temperature constant during the reaction is depicted in the Fig. 4. The heating system use the information obtained from thermocouple to attain the thermal stability required. In the first experiments was used the simplest controller, called on/off. This heating control system besides keeping the temperature in an adequate range, show instability during the time expend in the reaction. Another heating control system used was a proportional controller (P), acting when the temperature approaches 50°C.

Despite the apparent stability of the proportional controller (P), it was necessary to optimize the temperature control system. Aiming at making the temperature more stable a proportional-integral controller was used, which can evaluate the error in the temperature of each sample. According to the tests, the proportional-integral controller (PI) indicates a better solution to keep the temperature constant during the preconditioning of the samples.

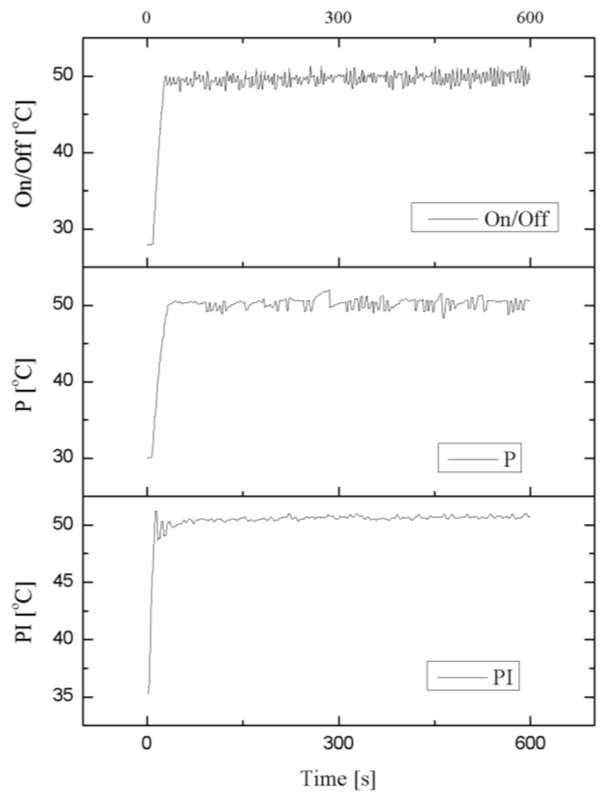

Fig. 4. Results obtained from the stability test of the temperature Controllers.

The MAX6675, a temperature sensor module, was used to evaluate the heating during the oxidative digestion process through a thermocouple attached in the microfluidic device. For the heating control test, a volume of the 3ml was heated during ten minutes in order to check the uniformity in the system over time. Using the first controller, on/off, a drift of 2°C was obtained and considered not good to apply in the system and to improve the heating control a proportional controller was tested and the drift decreased to 1.5°C. The temperature in both controllers do not show a good stability in the temperature set for the test. Hence, using the PI controller even with an over temperature in the heating start, the temperature drift was 0.3°C, being considered the controller more proper for the oxidative digestion process.

VI. CONCLUSION

In this paper is presented the design for a microfluidic oxidative digester for liquid samples. The device developed is an autonomous system that was manufactured using LTCC which is resistant to acids and bases. Also, the project provides thermal stability though a temperature controller. The great advantage of this device is the use of microfluidic channels which need small volumes of the reagents and samples, reducing the cost of the preconditioning step in the chemical total element concentration analysis. Also, the LTCC used in the manufacturing of the microfluidic oxidative digester offer important characteristics such as withstand high temperatures and resistance against strong acidic concentrations.

ACKNOWLEDGMENT

The authors thanks SENAI Amazonas for laboratories infrastructure and components acquisition, IEL (Euvaldo Lodi Institute) for financial support and for EPUSP (Polytechnic School of the University of São Paulo) for share laboratories and knowledge in the development of this work.

REFERENCES

[1] Srinivasan, V., V. K. Pamula, and Fair, R. B. "An integrated digital microfluidic lab-on-a-chip for clinical diagnostics on human physiological fluids," in, *Lab on a Chip 4.4*, 2004, pp. 310-315.

[2] Y. Paul, et al. "Design of microfluidic sample preconditioning systems for detection of biological agents in environmental samples," in, *Microfluidic Devices and Systems: International Society for Optics and Photonics*, 1998, pp. 252-259.

[3] M. R. Gongora-Rubio, M. B. Fontes,Z. M. da Rocha, E. M. Richter, & L. Angnes. "LTCC manifold for heavy metal detection system in biomedical and environmental fluids," *in Sensors and Actuators B: Chemical*, v. 103, pp. 468-473.

[4] R. Barry, D. Ivanov. "Microfluidics in biotechnolog," in, *Journal of nanobiotechnology*, 2004, p. 2.

[5] Bartels, Operating Manual for Micropump mp6-series, 2018.

[6] B. Henrik. "Theoretical microfluidics," vol. 18. Oxford: university press, 2008.

[7] D. V. Rossato, N. R. Schott, and M. G. Rosato, eds. "Plastics Institute of America Plastics Engineering, Manufacturing & Data Handbook," Berlin: Springer Science & Business Media, 2001.

[8] V. Abhay, et al. "An LTCC-based microfluidic system for label-free, electrochemical detection of cortisol, sensors and Actuators" vol. 182. 2013, pp. 139-146.

[9] N. Ibanez-Garcia, et al. "Continuous flow analytical microsystems based on low-temperature co-fired ceramic technology. Integrated potentiometric detection based on solvent polymeric ion-selective electrodes," in *Analytical chemistry*, 2006, pp. 2985-2992.

[10] DuPont GreenTape, Low temperature co-fired ceramic system manual.

[11] Autodesk Inventor 2019, manual, operation and computacional fluidc dynamics. Release "https://www.autodesk.com.br/products/inventor"

[12] Hosomi, Masaaki, and Ryuichi Sudo. "Simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulfate digestion" in, *International Journal of Environmental Studies* ,1986, pp. 267-275.