Prototype for chemical analysis and process intensification that is useful for research and teaching

Protótipo para análises químicas e intensificação de processos útil em pesquisa e ensino

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Abstract
This work describes the design, manufacturing and testing of a detection system useful to be applied with microTAS or other compact equipment, such as those needed for Process Intensification in Chemical Engineering. The detection is carried out by a Quartz Microbalance (QCM), based on Piezoelectric Quartz Crystals (PQC) of multiple frequencies, from tens of kHz to almost GHz. With this instrument, it is possible to detect particles and droplets in a gaseous flow, as well as vapors of volatile organic compounds. The system allows simultaneous measurement at five different points, and due to its modularity, such points can be positioned several centimeters apart from each other. The use in teaching is favored not only because of its low cost and modularity, and also due to its portability, i.e., its small size.

Keywords: Process Intensification. MicroTAS. QCM. VOCs. Particle Detection.

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Resumo
Este trabalho descreve o projeto, a construção e os testes de um sistema de detecção útil para uso em microTAS ou outros equipamentos compactos, como os necessários para Intensificação de Processos na Engenharia Química. A detecção é efetuada por uma Microbalança de Quartzo (QCM), baseada em cristais piezelétricos de quartzo (PQC) de múltiplas frequências, de dezenas de kHz até GHz. Com esse instrumento é possível detectar partículas e gotículas em um fluxo gasoso, além de vapores de compostos orgânicos voláteis. O sistema permite a medida simultânea em cinco pontos distintos e, devido à modularidade, tais pontos podem distar entre si de vários centímetros. O uso em ensino é favorecido não só pelo baixo custo e modularidade como também pela portabilidade, devido à pequena dimensão.


Introduction

Even though following different paths, at the end of the last century several branches of engineering pursued common goals. Thus, Chemical Engineering and Microelectronics focused on miniaturization, developing mainly Process Intensification (PI) and multifunctional equipment, respectively. However, whereas Microelectronics turned into more than ICs (Integrated Circuits) becoming the provider of tools for virtually any industrial sector, for instance with an immeasurably different forms of sensors, Chemical Engineering has developed a huge amount of instruments that concatenate different unit operations in a single equipment (HASEBE, 2004; CHARPENTIER, 2005; MATLOSZ & COMMENGE, 2002).

In Microelectronics, miniaturization and sensors production lead to the development of small and multifunctional equipment for chemical analysis and synthesis, known as Micro Total Analysis System (µTAS) and Lab on a Chip, respectively. The first one is emblematic on sample pretreatment and the second resembles a small laboratory; the peculiar thing about these devices is the dimensions, usually much bigger than the ones found in ICs (VAN MERKERK & ROBINSON, 2006). In Chemical Engineering the miniaturization of some unit operations is critical for obtaining PI optimization (PONCE-ORTEGA, AL-THUBAITI & EL-HALWAGI, 2012); thus, micromixers, micro heat exchangers, micro adsorbers and
specially microreactors and separators were developed (CHOVÁN & GUTTMAN, 2002) and most of the design of such devices are based in microchannels (GOMEZ et al., 2018).

Although the dimensions on PI devices are even bigger than the ones in µTAS or Lab on a Chip equipment, it exists a series of parts and pieces that are common on both approaches. Thus, in addition to the prevalence of continuous flow there are also the unit operations and mainly three separate and important parts: reactant/sample admission – manipulation/reaction and detection/production (ABIEV, 2020). Nonetheless, until now it is uncommon the use of microelectronic processes on the production of PI equipment. However, as state by Hessel, Sarafrraz & Tran (2020), Chemical Engineering process will be needed even in space and that will demand “in-situ resource utilization”, which will require “microfluidic approaches as prime tool to achieve process intensification”. The authors also emphasize that this perspective is already assumed by BASF Company. Teaching has been equally impacted by such trends and small low cost equipment was target (CLIPPARD, 2016; BOFFITO & RIVAS, 2020).

However, this intersection among PI, Microelectronics and Teaching presents a gap regarding nano, micro and macro technologies (RIVAS & KUHN, 2016). Nevertheless it also offers several advantages with equipment developed to meet these requirements: environmental (less residue), economic (low cost, less investment) and innovation (new processes and approaches) aspects.

In our former works we intended to develop low cost equipment and respective miniaturized unit operations with a focus on both research and teaching (SILVA, FURLAN & RAMOS, 2006; BERALDO et al., 2010; SILVA et al., 2010; PICIJIUNIOR, 2011; SILVA et al., 2012; LEITE et al., 2015). Therefore, this work aims to describe a prototype for chemical analysis and process intensification that could be used in research and teaching; the emphasis is given on detection subsystem since former works have already described unit operations and flow manipulation.

**Fundamentals**

This work is based on the concepts of Process Intensification, Miniaturization, µTAS and Continuous Flow, whether in analysis or in production processes, Prototype and Proof of Concept.
2.1 Process Intensification

Recently, Boffito & Rivas (2020) reviewed the PI definitions. According to them even the modern concept is not new and the idea could be found in patents since 1930s decade; however, in 1995, it was established the question of miniaturization, targeting a reduction of 100X or more in size of chemical plants while keeping other production indicators. The 21st century brought the idea for building such plants not only smaller but also cleaner and more energetically efficient, i.e., more sustainable. At the end of the last decade the focus changed, from the unit operation to the function of this unit; through this method, the increase in production wouldn’t necessarily be connected with the increase of reactant and energy consumption. Therefore, PI is an innovative and multidisciplinary approach to production. According to authors’ Web of Science review, the most frequent keywords are mass transfer, design, reactor and optimization. Hence, besides the simplest design solution of adding several unit operations in a single equipment, other possible attitudes might be increase mass and energy transfer by the development of new static mixer, compact heat exchangers, distillation columns and some reactors, in special microreactors.

For many stakeholders PI concept and implementation, in Chemical Processes and in all innovative technologies, are considered fundamental drivers to meet most of the United Nations, Sustainable Development Goals (SDG). In this context PI Education is cardinal and requires, among other things, virtual reality, laboratories, and simulation in addition to specific case studies (RIVAS\textsuperscript{a} et al., 2020; RIVAS\textsuperscript{b} et al., 2020).

2.2 Miniaturization, µTAS and Continuous Flow

Boffito & Rivas’ (2020) review also indicated the importance of miniaturization, especially of microreactors, on PI development. These devices favor green chemistry and flow chemistry, i.e, allow continuous production with energy and cost efficiency. The review also consider their dimensions in submillimeter range (“tubular reaction zone with ID < 1 mm”) and milli-reactors having diameters larger than 1 mm. For such dimensions the linear scaling, from microelectronics to PI, becomes straightforward (JANASEK, FRANZKE & MANZ, 2006). That was one of the major reasons for DNA analysis improvement leading to faster, more reliable measurements in a bunch of sciences, “medical diagnosis, criminal investigations, genetic research”. This also encouraged new developments on µTAS, DNA-chips and genomics. However, there is a duality, that Matlosz & Commenge (2002) called
information *versus* production. Whereas miniaturization favors obtaining chemical information for production purposes the use of miniaturization still have some constraints, for example laminar flow hindering mixing, plugging due to small dimensions and higher costs. Then, a possible approach is a distributed smaller scale production (‘mini-plants’), which increases safety versatility. These considerations are similar to those presented by Hessel, Sarafranz & Tran (2020) to support the importance of microfluidics devices in future space installations and habitats.

Accordingly, since the bigger dimensions of such devices allow the production using conventional tools, and a variety of different materials could be addressed without any use of costly environment, like clean rooms, which directly impact the overall cost, it is possible obtaining low cost devices (BOJANG & WU, 2020). Gomez et al. (2018) indicated the several advantages of microfluidics continuous flow devices, in analysis and in synthesis, due to the “high surface-to-volume ratio, small thermal inertia, fast temperature changes, easy adjustment of residence times, and production of emulsions and suspensions with monodisperse distribution”. However, considering the high costs for manufacturing of silicon devices, suggest the use of Low Temperature Co-fired Ceramics (LTCC). Moreover, these dimensions and distinct substrates allow the production of 3D structures, which could diminish some secondary effects, such as capillary ones. A singular example is the use of curved 3D microchannels for mixing (QAMAREEN, ANSARI & ALAM, 2022; RASOULI, 2018), an alternative purpose for educational purposes is also feasible

Regarding detection of separated analyte (in chemical analysis) or produced material (in synthesis) a plethora of sensors exists, which means each problem and corresponding setup must be evaluated separately. This work uses a Quartz Crystal Microbalance (QCM) for detection, technique based on the frequency variation caused on a Piezoelectric Quartz Crystal (PQC). If an oscillator is built using a PQC as its frequency determinant, that frequency could be changed if material is adsorbed onto the surface of this PQC. Sauerbrey’s Equation (Eq. 1) describes this variation and states that mass variation is directly proportional to frequency variation; thus, PQC works as a sensor for small mass variations, in the order of nanograms (LEITE, 2016).

\[
\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \Delta m
\]  

(1)
Where:

\[ \Delta f - \text{change in oscillation frequency due to the mass variation (}\Delta m\text{) on the active surface area (}A\text{);} \]

\[ f_0 - \text{natural oscillation frequency;} \]

\[ \rho_q - \text{density and} \mu_q - \text{shear modulus of the PQC, respectively.} \]

### 2.3 Simple Prototype and Proof of Concept

This work considers as a prototype a fully functional equipment even if the dimensions are reduced when compared to similar commercial ones (LIMAD, 2019). Proof of concept provides insights on the feasibility of the proposal (device). A quantitative evaluation is not mandatory; however, an overview of the strengths and weaknesses of the proposal exists. This is generally accomplished by describing how the instrument operates in a specific example (ALVES, 2011).

### Materials and Method

This work is an exploratory and applied research based on proof of concept and considered the constraints, as indicated in the Introduction item, of Chemical Engineering, Microelectronics and Teaching. Figure 1 shows a conceptual map for this approach and, as could be notice in the figure, these constraints also determine the criteria used on equipment development:

- **Modular:** keeping important parts mounted separately allows an easy upgrade and a didactic approach during the use.
- **Useful for miniaturized structures, also known as mesostructures, it keeps the size of equipment small (portable) and favors process intensification in two ways: leading to versatile forms of joining unit operations and increase versatility, allowing the easy change of such structures.**
- **Commercial parts and pieces from the market keep the price affordable.**
- **Use of safe reactants is mandatory for didactic purposes but also for green chemistry, one of the premises of PI.**
- **Analysis of complex samples implies in sample pretreatment, which could be made by the proper choice of these mesostructures.**
- **Multifunctional:** changing not only the structures but also the detection system is possible to attend different problems.
The equipment, named MiniLab (LEITE, 2016), could be observed in Figure 2A and the three main parts (admission-manipulation-detection) are depicted with inserts whereas Figure 2B presents equipment schematics and properties. The admission is based on plastic material and mainly depends on a flow controller and low-cost valves. Manipulation uses a XYZ table, which allows the use of 3D mesostructures adapting the equipment to changes not only their size but also on their inlet/outlet positions. However, the use of other inexpensive positioning system would present the same results.

Regarding the detection system, the choice was a QCM setup, i.e., a PQC array used as sensors. The main advantages of its usage are comprehensively evaluated previously (LEITE, 2016): portability (small devices and setup); low cost; easy implementation in several distinct setups; sensitive for drops and particles presence; as long as the PQCs surfaces are modified properly, useful for detection of compounds; quantitative or qualitative analysis; low detection limit and high sensitivity. In contrast, QCM presents low selectivity, what could be managed by the use of PQCs array and the emblematic example is its use in electronic noise systems. After the choice of the detection system, some criteria were established:

- Detection of particles, drops and volatile organic compounds (VOCs).
- Array of 5 PQCs working simultaneously, but eventually each PQC has to present independent movement.
- Low cost, small, portable, and independent device, which means that can be used aside the full equipment (detachable).
- Developed as open-source software and free hardware (can be used without property issues).
- Versatile, which implies user chooses previously the unit operation and proper sensor (PQC surface modification adequate to monitoring the unit operation).

Figure 2 - MiniLab (equipment) photo (A) and (B) schematics with the forming parts (admission-manipulation-detection) proper signaled.
Source: The Authors
In principle, QCM electronics can be developed using three main possibilities: microcontrollers, Arduino series or PIC (Peripheral Interface Controller) from Microchip, or MyRIO-1900 platform and LabView software, from National Instruments®. Arduino is a low cost but less precise option, MyRIO is professional but more expensive; therefore, this work used PIC 18F4550 and accessories.

The electronic project uses PROTEUS® software and its tools; therefore: 1) PQC behavior was simulated using "clock generator", 2) virtual terminal tools were needed for the simulations of internal and external communications, 3) commpm e usbconn tools allowed communication with other software, such as "Free Virtual Serial Ports Emulator", which assures the reading and writing of external devices.

After the electronic simulation, the project is virtually tested using open source software, Putty®, which allows certify communication with external devices and, after that, using software Python®, the data manipulation, i.e. reading, organization and generation of data files in CSV format, i.e., the data can be manipulated in any personal computer.

Circuitry uses only commercial components and manufacturing was obtained with conventional electronic setup and tools. Moreover, the detection system was also compared to a commercial instrument (frequency meter, Instrutherm®, FD 990). Tests considered the following indicators:

- Frequency range: using PQCs with distinct frequencies (2.4; 4; 7 and 10 MHz) and a commercial equipment to check upon the measurements of the developed equipment.
- Precision, accuracy, sensitivity: meaning mainly the detection limit achieved by the instrument.
- Reproducibility: every test was made in triplicate.

Manipulation of chemical vapors and particles were described elsewhere (SILVA, 2010).

**Results and Discussion**

This section presents project, manufacturing, and tests of the detection system.

**4.1 Project, Manufacturing and Calibration**

The detection system is composed of three parts:
- A PQC case for 1 inlet/outlet gaseous samples (Figure 3A) or a manifold if 5 inlet/outlet are used (Figure 3B); the main difference from each arrangement is only the existence or not of a common base. Nonetheless, a single PQC case allows more manipulation, i.e., the sensor can be positioned several centimeters apart from the admission part (Figure 2A).
- PQC with electronics (Figure 2A).
- Acquisition setup and Data manipulation (Figure 2A).

Figure 3 - (A) schematics of PQC case for independent mode or (B) Manifold for 5 inlet/outlet: schematics and photo.
Source: The Authors

All circuit diagrams, as simulated and virtually tested in Proteus®, are presented in Figure 4 (A to D). The circuit is composed of 3 main function blocks, which parts are count system set; interlock and processing system, in addition to two support blocks, voltage source and oscillators set.

The voltage source furnishes the adequate current and tension to feed the whole system and comprises a 5V/2A switched source together with capacitors distributed on the printed circuit board. The oscillators set is based on the 74ls04 IC and only three inverting logic gates is required to attend one PQC; therefore, three IC are needed. Moreover, each oscillator requires a 10nF ceramic capacitor and two 470 ohm resistors attached to the respective PQC (Figure 4A). These gates are connected directly to the crystal, what generates a square wave signal using TTL format. This signal is the input in one counter in the count system set.

The counter system set is comprised by 5 counters blocks. Each block is composed of 8 units of 4-bit counters, which are responsible for recording the pulses coming from one oscillator. This set uses the 74ls393 IC and, after some pre-determined time interval is achieved, the output data of this counter is transferred to the microcontroller (Figure 4B). This transfer action depends on the interlock and the 3-state because all counters are connected to the same microcontroller input segment. This interlocking is composed of a 74ls154
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Moreover, one central microcontroller (PIC 18F4550) is responsible for synchronization and command of all the main function blocks. This microcontroller also manages the pulse sampling interval, readings and reset of all counters and the interlocking main commands (Figure 4D). Since all data is on its management, this microcontroller, after the string, data is sent to the computer software. This transmission uses USB port and USB-CDC logic, which assures that the proprietary software and hardware will be linked as a serial port.

![Prototype schematic](image)
All the components are positioned on a double layer PCB board (Figure 5A) and assembled in a separate case, which allows portability. The software was developed in Python and the FrontPage is depicted in Figure 5B. Its main characteristics are “pyserial” library, adequate to serial ports, and “tkinter” library for graphic layout, which required Spyder IDE. The software FrontPage possesses several distinct attributes, such as data collect and storing. The collection previously requires the choice of USB port (ComboBox), i. e., the system has one interlock that demands this choice and connection for the beginning of a new measurement. This parameter set assures that all measurements will be safely stored. A series of other interlock commands also impedes misbehaviors, for instance it is not possible to close the software before data saving. Online graphic manipulation is also possible; however, since the saved data is maintained in CVS format any other commercial software could be used.
The system was certified using the commercial instrument and comparing both measurements. As it could be seen in Figure 5C a good linear correlation exists, with the error occurring in the range of 1 Hz.

Figure 5 - Mini Lab: (A) Acquisition Data; Manipulation Data showing (B) Software FrontPage and Calibration using (C) PQC measurements with (abscissas) commercial equipment (ordinates) and the developed one.

Source: The Authors
4.2 Detection Tests

4.2.1 Particles

Tests used starch, 50 µm, and cyclone microstructure (LEITE et al., 2015) inserted in the manipulation area. During the experiment, the microstructure behavior was filmed and the time for first appearance of starch particles was compared with QCM measurements; Figure 6 shows typical results. QCM measurements (Figure 6A) shows a constant line (the apparent noise is due to the low variation on PQC frequency) up to the cyclone disability, owing to the amount of starch admitted in the microstructure; at this point the frequency variation increases and, at the same time (Figure 6B), PQC shows particles on the surface, it is worth noting that frequency variation does not came to the initial value since these particles adhere to the PQC surface.

![Figure 6 - (A) QCM measurement: frequency variation as a function of time and (B) PQC appearance (filming)](image)

Source: The Authors

4.2.2 Drops

Tests used a spray microstructure, also described elsewhere (SILVA, 2012), inserted in the manipulation area and filming; Figure 7A shows a typical result. Although suddenly there is a huge change on frequency, consistent with spray drops hitting the PQC surface, as can be seen in the insert, few moments earlier there are also some small variations. In other words, even tiny drops that precede the main spray jet were detected too.
4.2.3 Compounds

Vapor detection could be done using the manifold in independent mode (Figure 3A), and a direct insertion, since the PQC surface was changed using adsorbent thin film. Figure 7B shows typical behavior of 1µl acetone vapor reaching a modified PQC surface; that result is in good agreement with similar results previously obtained in commercial equipment (LEITE, 2016). Moreover, considering the small amount of vapor needed for detection, this system could actuate in ppm range or less; on the other hand, the selectivity depends on the surface modification and, as can be seen in Figure 7C, as expected, distinct surface modification leads to different results.

Conclusions

This work proposes a small, useful equipment in research and teaching. The referred device has a detection system that is able to perceive particles, drops or VOCs compounds.
present in a gaseous flow. The sensitivity of such detection is ppm range or less and, with proper surface modification, selectivity could be improved.

PI developments focus on sustainability through different approaches, for instance various unit operations coligated and less consumption of raw material and energy. The equipment is modular and assembled in a manner that favors quick exchange or addition of unit operations (through XYZ Table), the small amount of material handled leads to minimum residue, if so. This easiness on reactant manipulation and disposable increase equipment safety and turns the device quite resourceful for educational purposes, small size and low cost allow its use also in expository classes, not just laboratory demonstrations; therefore, specific PI case studies could be addressed. The continuous flow approach and 5 simultaneous sensor measurement also attend the PI principles and, for educational purposes, can emulate a Chemical Engineering mini plant.

The whole equipment can be produced using conventional tools and, more specifically for detection system, all parts and pieces are easily found in commercial places.

References


RASOULI, M. et al. Multi-criteria optimization of curved and baffle-embedded micromixers
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