Automation of Secondary pH-Measurement System at National Metrology Institute of Colombia.

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***Abstract*— As a fundamental part to assess traceability and the quality of pH-measurements carried in analytical laboratories in Colombia, National Metrology Institute of Colombia-INM has developed and implemented a secondary pH-measurements system that allows certification of reference materials or standards; in order to generate the best metrological tool required to be the reference and to make measurements of pH, in industry and academia in the country. To optimize this type of determination by secondary pH-measurement system, an automatic program based in LabVIEW was developed, this program configures and performs the operation of integration from measuring instruments for data recording and controlling process in real-time, which is a step necessary for making easy the subsequent data recording and experimental data analysis.**

Keywords*— *pH-measurements, automation system, certified reference materials, metrology, traceability of measurements Introduction (*Heading 1*)

I. Introduction

The most widely used measurement for the acidity or alkalinity of solutions is pH, this is a measure of hydrogen ion concentration. The pH scale ranges from 0 to 14. Aqueous solutions at 25°C with a pH less than 7 are acidic, while those with a pH greater than 7 are alkaline. A pH level of 7.0 is defined as neutral because the concentration of H3O+ equals the concentration of OH− in pure water. The pH, or hydrogen potential (potentia Hydrogenii), is defined by equation 1 (Sørensen equation), as the negative decimal logarithm of the molar activity of the hydrogen ion (aH) in aqueous solution [1-2].

$$pH = -log\, a_H \qquad (1)$$

pH measurements of real samples are performed by potentiometry using a glass electrode connected to a digital pH meter, which must be calibrated using reference buffer solutions. These measurement results require the establishment of a metrological calibration hierarchy linking the quantity in the sample to a unit in the International System of Units (SI). For pH, a traceability of measure can be established by calibration using primary reference buffer solutions, for which the pH values are obtained by utilizing the internationally recognized measurement procedure. This procedure, called primary pH measurement, is based on potentiometric measurements for electrochemical cells, called Harned cells. It is common that these primary standards are too expensive for analytical laboratories. In consequence, laboratories can achieve traceability by means of secondary reference buffer solutions. These solutions can be standardized in comparison with primary buffer solutions using a procedure that employs cheaper instrumentation. The secondary pH measurement which used electrochemical cells, called Baucke cells. This standardization procedure usually makes use of a differential potentiometric cell with a single junction separating two half-cells: one contains the primary buffer solution and a hydrogen electrode, and the other contains the secondary buffer solution and another hydrogen electrode [3].

The National Metrology Institute of Colombia-INM had developed the secondary pH-measurements system in order to certify the reference materials that will be to assure traceability to International System of Units-SI by means of an associated uncertainty, with the aim of to obtain quality assurance of measurement results. The system is shown in figure 1. It consists of a thermostatic bath (a), a glass cell called type Baucke [4-5] (b), a voltmeter (c) [6], a thermometer (d) with sensor Pt-100 (e)[7]; and hydrogen supply (f). To optimize pH-measurements with the Secondary Measurement System, automation was developed based on the programming environment by National Instruments LabVIEW [8].

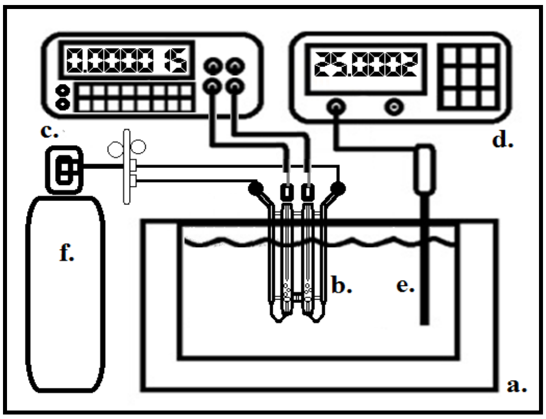

Fig. 1. Secondary pH-measurement system scheme.

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II. MEASUREMENT SEQUENCE

The Automation of secondary pH-measurement system at National Metrology Institute of Colombia was developed in LabVIEW software with the graphic programming environment from National Instruments, which is focused on developments in engineering and teaching.

The LabVIEW program was designed to simulate the performance of a real instrument by means of programmatic virtualization called Virtual Instrument-VI, which allows develops of modular steps called Sub-VI. These can be used for other applications, to improve developments, to provide advantages for updates generates, or extensions. In this way, it is possible to bring broad scalability of components. Applications developed in LabVIEW are divided into two main parts, a front panel (or the user panel) where all controls are displayed and then the interface is developed; the other part is a rear panel (or block diagram panel) where the application algorithm is developed in a graphic environment.

The graphic programming environment helps to create applications where can graphically visualize each aspect of the algorithm development, the data flow, programming loops, the hardware configuration, and other aspects, which are of complex visualization in an environment as code-line classic programming.

LabVIEW is widely used for the development and automation of measurements in different laboratory applications, because it facilitates the communication, and the synchronization of different equipment, and different manufacturers by means of the use of standard commands such as Standard Commands for Programmable Instrumentation-SCPI [9]. The development of the automatic pH-measurements for secondary system works with the advantages and benefits provided for LabVIEW, which allows the program will be able to record, analyze and evaluate the raw pH-measurement data, these values are determined with several steps. In this order of ideas, it is necessary to set up measuring instruments according to the following sequence:

(1) Setting parameters of measuring instruments

(2) To perform temperature measurements into the thermostatic bath

(3) Measure a potential difference generate into the glass cell between two solutions. Figure 2 shows configuration to voltmeter and cell. The cell has two compartments, in one is set an item under test and another is set a reference

(4) To record data for future analysis

Notes: - Steps (1) and (2), are repeated until to accomplish predefined temperature control

- Step (3) is performed until to accomplish data stability such as that in Figure 3. Before you begin to format your paper, first write and save the content as a separate text file. Complete all content and organizational editing before formatting. Please note sections A-D below for more information on proofreading, spelling and grammar.

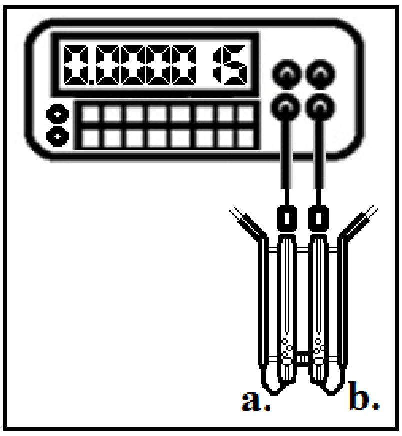


Fig. 2. Diagram configuration of voltmeter and cell

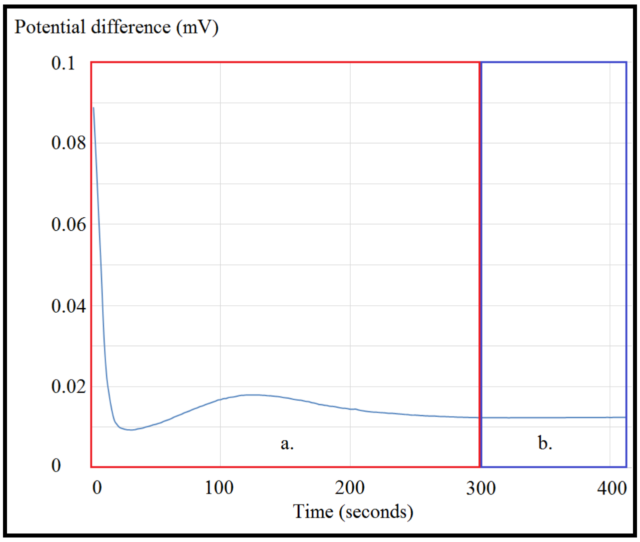


Fig. 3. The potential difference measuring curve. a. signal stabilization period b. data stability

A. Abbreviations and Acronyms

The multimeter Keithley 2700 had an interface General Purpose Interface Bus-GPIB and Standard Commands for Programmable Instruments-SCPI. Commands used to potential difference measurements by the secondary system are presented in Table 1.

TABLE I. COMMANDS USED IN VOLTMETER.

Commands used in voltmeter		
Operation	***SCPI Code***	***Description/meaning***
Identify device	*IDN?	This command returns a response about general information about the device such as serial number, model, and manufacturer.
Capture channel # measurements	MEAS?(@10#)	The text of this command is short for measurement and it returns a measurement made by the instrument in a defined channel.

B. *Thermometer configuration*

The thermometric bridge ISOTECH milliK had an interface serial RS-232 with connector DB-9 null-modem, and also SCPI commands. Commands used to temperature measurements by the secondary system are presented in Table 2.

TABLE II. COMMANDS USED IN THERMOMETER.

Commands used in voltmeter		
Operation	**SCPI Code**	**Description/meaning**
Capture channel 1 measurements	MON1?\s2\r\n	The text of this command is the abbreviation for monitoring and returns a reading of the instrument in the indicated channel. It differs from MEAS since it does not command the instrument to take a measurement. The instrument is in constant measurement and command MON takes only the reading.
Identify device	*IDN?\r\n	This command returns a response about general information about the device such as serial number, model, and manufacturer.

III. RESULTS AND DISCUSSION

The pH-measurement process by secondary system is developed according to Figure 4. This algorithm contains two main parts: in the first part (a), a general-configuration of system is made and another part (b), measuring-cycles are carried out.

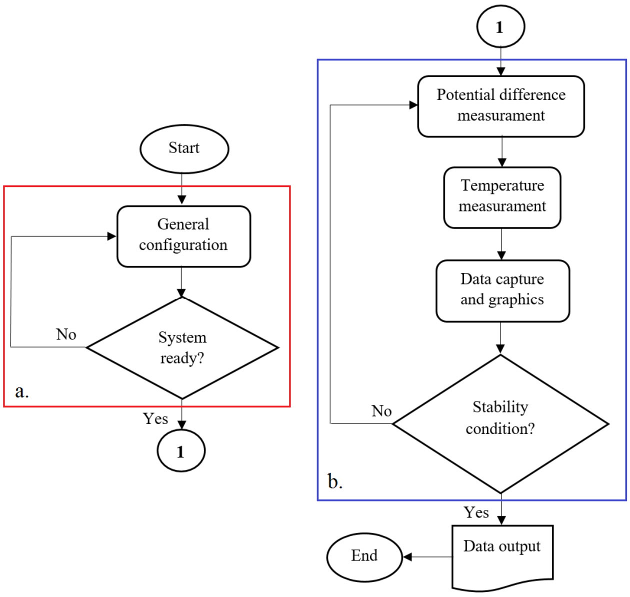


Fig. 4. Algorithm flow chart

In the stage a., the general system configuration of auto-detection instruments is realized [8], the idea is to select the measurement channel on the voltmeter. After that, the stability control parameter is settled, if it is generated an event that affects the normality of process, a message is sent for indicating to user failure reason. Contrary, if the system is worked well, it will move to the next automatic measurement phase.

In the stage b., it is settled default options (such as number de cycles, the data used to calculate the average, etc.) that can be modified by the user before to start measurements. The frontal panel of software developed is show in figure 5. In this panel, the user starts the program and the data is recorded. The software provides measurement values, graphics and the control evaluation of the potential difference measurements and temperature. If the control condition, or stability parameter, does not comply the program continues through to find this value defined, and then the program stops, the data is organized in a flat-file.

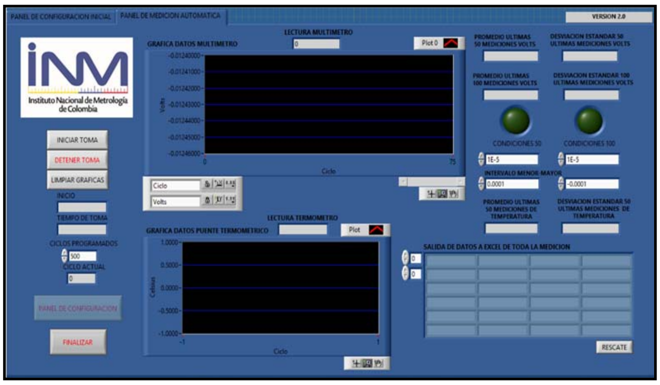


Fig. 5. The front panel of software

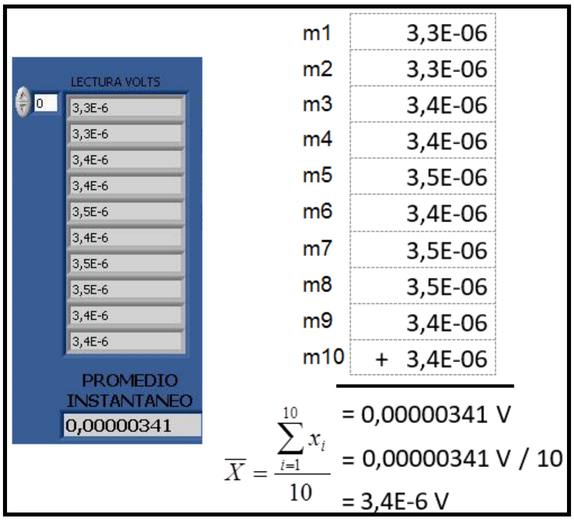
IV. RESULTS AND DISCUSSION

To ensure performance, it is necessary to validate the software with the aim of protecting information and to ensure that this is not modified by its execution [10-11]. This validation is made according to following points:

1. To verify the commands from instruments, transmission and registration of data

Fig. 6. Comparison between software configuration for measuring on channel no. 1 and measured data from equipment in channel no. 1.

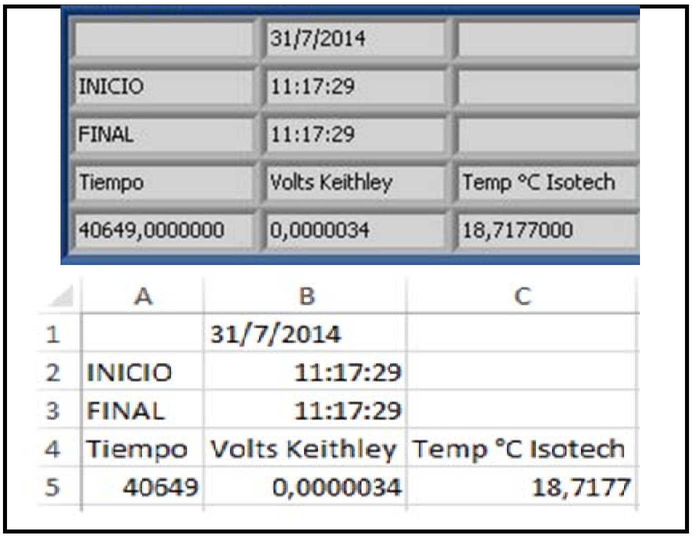
2. To verify that data recorded are correctly proceeded by internal mathematical operations



$$\overline{X} = \frac{\sum_{i=1}^{10} x_i}{10}$$

Fig. 7. Calculations processed by the software and calculations desktop-based testing.

3. To verify that data recorded are correctly proceeded by internal mathematical operations



	31/7/2014	
INICIO	11:17:29	
FINAL	11:17:29	
Tiempo	Volts Keithley	Temp °C Isotech
40649,0000000	0,0000034	18,7177000

	A	B	C
1		31/7/2014	
2	INICIO	11:17:29	
3	FINAL	11:17:29	
4	Tiempo	Volts Keithley	Temp °C Isotech
5	40649	0,0000034	18,7177

Fig. 8. Comparison between software values and exported values.

V. CONCLUSIONS

The secondary pH-measurement system automation allows reducing human intervention in measurements and data recorded, that will be allowed to achieve better stability and repeatability.

The validation of process was successful; the results from automatic measurement do not have alteration or errors.

The system is designed with modular programming sub-VI (Virtual Instrument), whereof it is possible to do scalability and modularity, with other instruments or measurement techniques

The secondary pH-measurement system at INM (equipment and automation software implemented) had participated with satisfactory results in comparisons SIM.QM-K91 between other national metrology institutes in the world. Figure 6 [12].

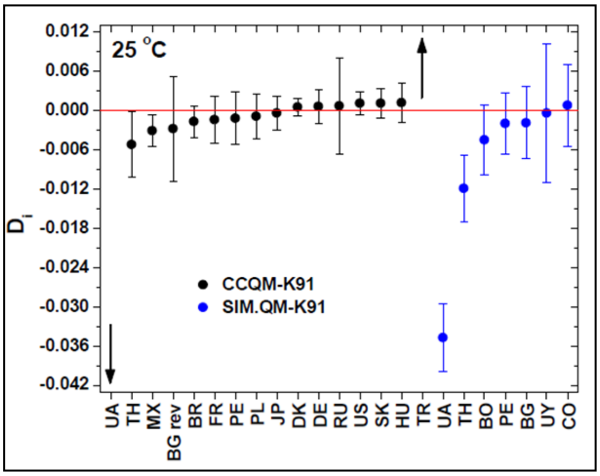


Fig. 9. D_i. Degrees of equivalence between SIM.QM-K91 and CCQM-K91 pH-measurement (CO: Colombia)

FUNDING

This study was supported by National Metrology Institute of Colombia under project SMQB-I-3.

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