Development of Sensor Calibration against Standards using Measurement Software TestPoint^{TM}-CEC and Application to the Verification of pH Electrodes

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Summary: The acquisition, processing and presentation of data from many commercial devices have been simplified by use of personal computers (PCs) and effective software in last decades. As compared to text-based languages, such as BASIC, dataflow programmation (LabVIEWTM) and graphical programming (TestPointTM) have been developed and widely used in diverse scientific fields. Here, TestPointTM is used to control via IEEE-488 interface a system voltmeter; pH measurement is a master variable in analytical chemistry and environmental studies. For precise and accurate measurements of pH, timely verification and calibration of pH electrodes are essentially required. However, the sensitivity of most commercial pH-meters (0.1 mV) is not high enough to check the deviation with respect to Nernst's law. With this combination of a high resolution voltmeter and graphical programming, data are acquired and processed as follows: a moving average is computed to check if equilibrium is attained and statistical tests are performed to define the confidence interval of the slope of the regression straight line. This allows the user to compute the deviation from the ideal law, generally statistically significant and to verify pH electrodes against NBS standards, according to IUPAC recommendations. A control chart can be easily drawn to define when the electrodes must be replaced. The method and the code can be easily modified to calibrate other sensors.

Introduction

Conventional manual acquisition, analysis and presentation of the data from electronic devices are very laborious and time consuming. So, in last decade, commercial measurement devices are largely controlled by the Personal Computers (PC) and an integrated efficient programming software package. In the beginning, preferred text-based languages in research institutions (Basic, C, Fortran and Pascal) were introduced to develop simple programs and control the instruments. But development of user interface in these conventional text-based languages is normally much time consuming task. Additionally, it takes much time and experience to learn programming, to get an overview of libraries with the graphical components and their use and making changes in subroutines or add-ons. Graphical Programming Environments (GPEs) such as TestPoint^{TM} (a ^{TM} is a trademark of Capital Equipment Corporation) by CEC [1], LabVIEW^{TM} by National Instruments [2], Delphi [3] and VEE by Hewlett Packard [4] have been available for few years. Learning and working with these packages is relatively easy and rapid.

Graphical Programming Environments (GPEs) allow the user to control instruments without writing directly the codes. This ensures the correctness of the syntax. Loops, interfaces with data acquisition (RS232, IEEE-488…..), control panels, exportation of results as spreadsheets, presentation of results on screen are some of the general features of GPEs. Features and prices of GPEs are different from each other. In LabVIEW^{TM}, graphical programming codes are shown in graphical diagram which makes it different from other GPEs [5]. In TestPoint, each object in the panel allows the user to perform a definite set of actions by just dragging and dropping and shows the programming codes alike to text-based languages (Fig. 1 and Fig. 2).

In the TestPoint^{TM} environment, there is an operational panel (Fig. 1.C and 1.D), of every panel in "Object window" (Fig. 1.B), which appears according routines arrangement. Main operational panel (Fig. 1.C) appears automatically when we change from ``Mode=Edit'' to "Mode=Run" in the toolbar and operational panels of others like "sample info." (Fig. 1.D) appears according the order of written program. In an operational panel, various tasks are performed: entering of data, view of data acquisition, making a graph *etc*., with the help of various pushbuttons and we proceed to next step. So, one can work with TestPoint^{TM} without going in programming window. Programming window appears when we right click on button "Run" in the "object window" and choose "action list" (programming window is shown in Fig. 2.D).

Learning and working with TestPoint-CEC, as other graphical languages, is, no doubt, relatively easy than text-based languages but for any programming language, it necessities learning. It can take 1 -2 months to understand the logic of Testpoint-

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CEC and to construct a program for first application. TestPoint[TM] is widely used in various scientific fields [6, 7]. Working with TestPoint[TM] environment and advantages and limitations of TestPoint[TM] have been briefly discussed in literature [8, 9].

pH Measurement

The pH measurement is a master variable not only in analytical chemistry and environmental studies but also in medical sector where variation of 0.01 of pH of blood can result in serious metabolic problems [10]. The pH is related to the activity of H^+ ion in a solution and defined as:

$$pH = -\log a_{H+} = -\log (m_H . \gamma_H / m°)$$

where, a_{H+} is the activity of H^+ ions, γ_H is the coefficient of activity of H^+ ions, m_H is the molality

in mol/kg of H^+ ions and m° is the molality at standard state. Strictly speaking, from this definition, pH is the measurement of the activity of a single ion species and its measurement is impossible [11, 12]. The operational definition of pH is thus based on the measurement of the difference between the pH of an unknown sample, pH_1 and the pH of a standard , pH_2, as follows [13]:

$$pH_1 = pH_2 + \{(E_2 - E_1) / (\ln 10 . RT/F)\}$$

where R is the gas constant, T the thermodynamic temperature and F the Faraday constant. E is the electrometric force (e.m.f.) measured between a reference electrode and a measurement electrode. This potential difference is linked to the activity of H^+ ions by Nernst's law:

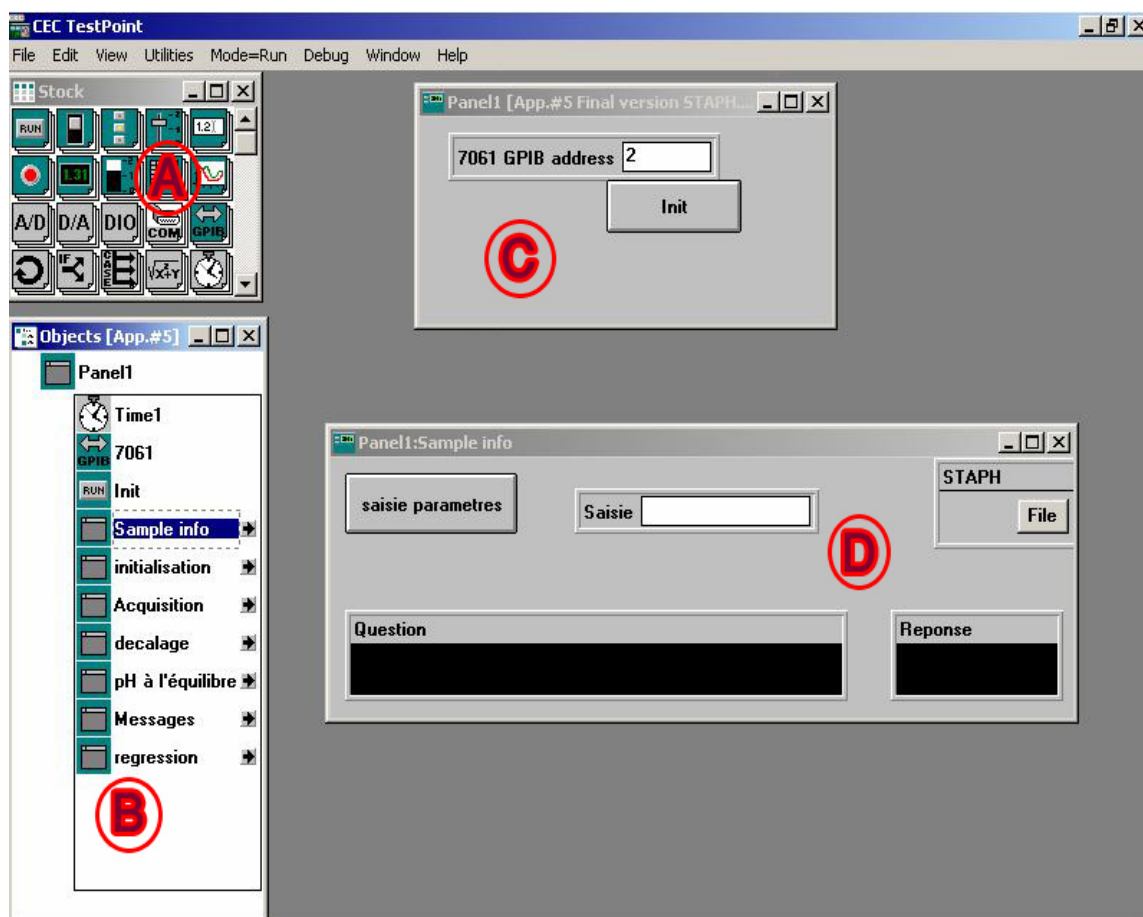$$E(pH) = E_0 + \{(\ln 10) . RT/F . (\log a_{H+})\}$$

Fig. 1: Window for user and non programmer in TestPoint[TM] environment. A. Stock; B. Object window; C. Main operational panel; D. Sample information panel.
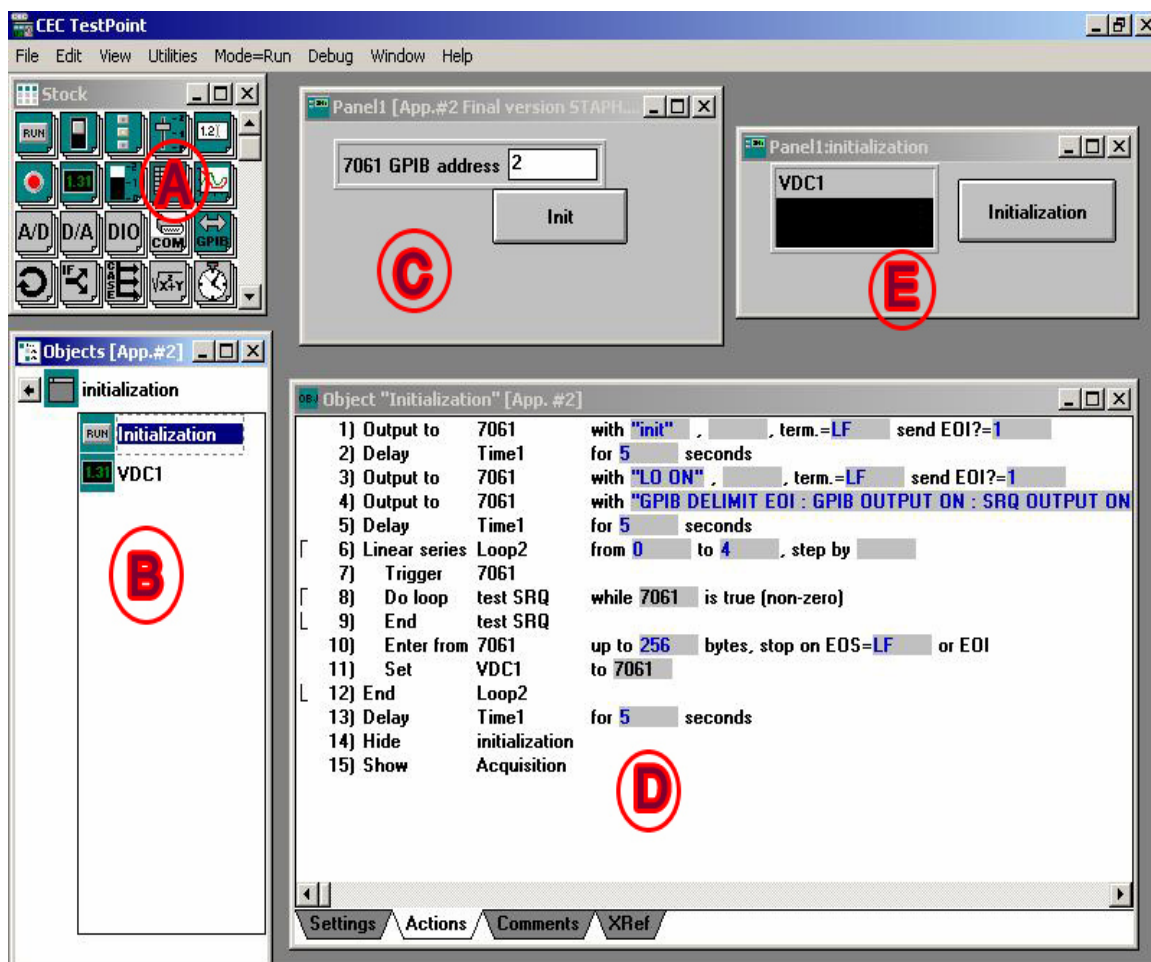
Fig. 2:   Programming window in TestPoint^{TM} environment. A. Stock; B. Object window; C. Main operational panel; D. Voltmeter initialization program; E. Voltmeter operational panel.

The only two independent variables in above equation are temperature and pH. Because both of these will affect the voltage output of the electrochemical cell, temperature compensation in the calibration is very important for pH measurements. Although E_0 is a constant, its value varies between individual electrodes and with temperature. A pH electrode, such as the most commonly used glass electrode, shows neither SPAN error when it produces 59.159 mV per pH unit and nor OFFSETS error if it produces zero mV when the pH of the sample is the same as the pH of the inner filling solution, usually a pH = 7.00 buffer. This means electrodes should show an ideal behaviour without any deviation from Nernst's law. Actual electrodes deviate from ideal behaviour. Moreover, as electrodes are used or stored for long periods they will experience some degradation from the new electrode specifications. OFFSETS will change and SPAN error will increase; i.e., the slop will become smaller. So, timely verification of pH electrodes

should be carried out to avoid unknown errors in final results.

Normally verification and calibration is carried out with commercial pH meters. The pH electrode has internal resistance in the range of 10-100 MΩ [14-16]. To reliably measure potential, voltmeter must have internal resistance at least 100 times larger, while most digital meters available have resistance in the range of 1-10 MΩ, thus they are not effective for verification or calibration. Accordingly, sensitivity of most commercial pH-meters (0.1 mV) is not high enough to check the deviation of pH electrodes with respect to Nernst's law.

The objectives of this paper is to discuss the principle of using TestPoint^{TM} and to describe a simple program developed in TestPoint^{TM} integrated with a high resolution voltmeter to calibrate sensors against standards. More specifically, it is developed to verify pH electrodes according to IUPAC

recommendations. This program can be very useful for every analytical and geochemical laboratory for timely verification, calibration or replacement of a pH electrode. It can be obtained at no cost from our laboratory and can be easily modified to adapt to other sensors' calibration (*i.e.* redox potential electrodes, temperature sensors, electrical conductivity measurement electrodes).

Results and Discussion

A regression equation and its R^2 value for the measurements taken with 4 years old pH electrode are presented in Fig. 3. The results show that deviation of voltmeter readings (Volts) from calculated readings (volts) for ideal Nernst's law is minimum near pH value 7 but maximum as we approaches to acidic pH values or very alkaline pH values. The results shows a very good r^2 value which indicates a good relation (0.9997) between pH of standard solutions and voltmeter readings but the correlation coefficient is not a good indicator of the deviation of calibration curve from the ideal behaviour. When the deviation of pH electrode from Nernst's law was calculated by estimating alpha (α) value as follows:

$$\alpha = m_{exp.} / m_{theo.}$$

where $m_{exp.}$ is the experimental slope obtained from regression equation and $m_{theo.}$ is the Nernst's slope obtained from the following equation:

$$m_{theo.} = (\ln 10).RT/F$$

In the calibration obtained here by TestPoint , $m_{exp.}$ = -0.055957 V/u.pH, while $m_{theo.}$ = -0.059159 V/u.pH, hence the alpha value obtained was 0.945. The confidence interval on the slope, at probability level 0.01 was [0.05592 - 0.05600], so that the experimental slope was highly significantly different from the theoretical slope. The alpha value should be between 0.98 and 1 for good precision measurements. This meant our pH electrode must be replaced by a new one.

This procedure was repeated for a newly bought pH electrode and, similarly, a fitted regression equation is shown in Fig. 4. Nominal deviation of a new pH electrode from the ideal Nernst's law makes the R^2 value equal to 1. The alpha value obtained was 0.992 which is highly acceptable value. So, the results show that this new electrode is reliable and accurate for pH measurements.

So, this programme developed in TestPoint[TM]-CEC with statistical approach and using high resolution voltmeter allows not only the calibration and verification of sensors (like pH electrodes) against standards but also helps us to maintain the record of sensors performance with time. This record can be used to make decisions for the replacement of degraded sensors.
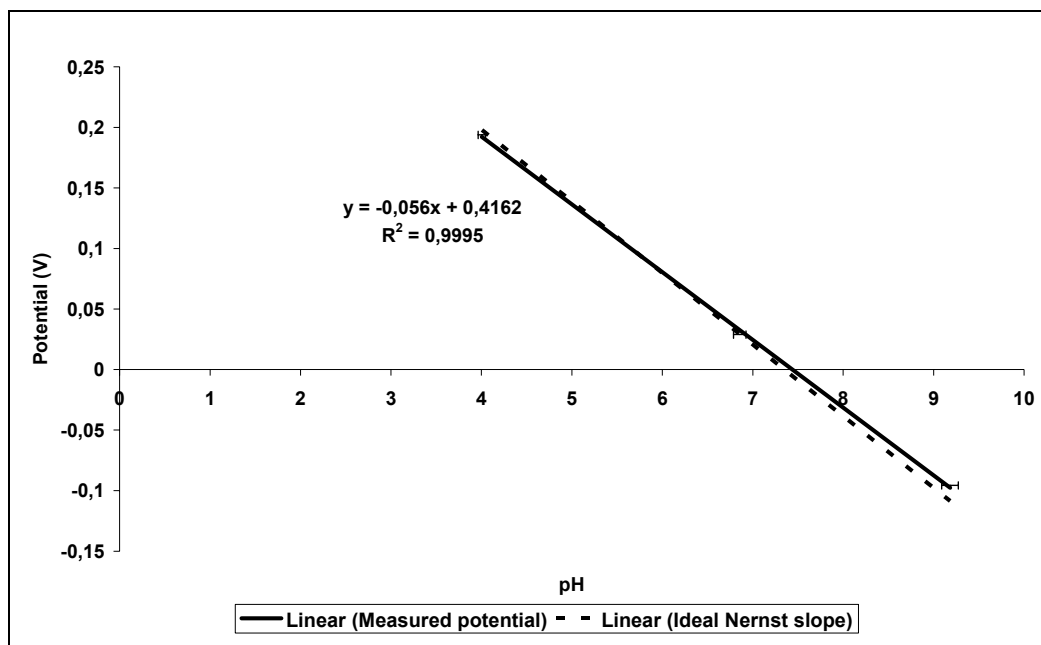

$$y = -0,056x + 0,4162$$
$$R^2 = 0,9995$$

Linear (Measured potential)   Linear (Ideal Nernst slope)

Fig. 3:   X-Y plot of pH and Voltmeter reading (Volts) for a 4 years old pH electrode.
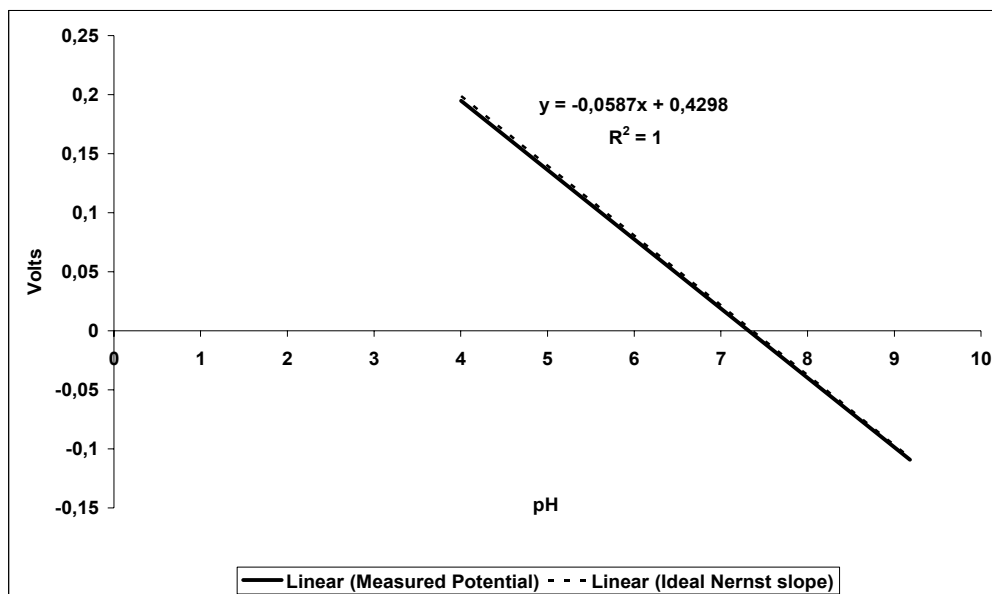
$$y = -0,0587x + 0,4298$$
$$R^2 = 1$$

Fig. 4:   X-Y plot of pH and Voltmeter reading (Volts) for newly bought pH electrode.

Experimental

Organisation of equipments in our experiment is shown in Fig. 5. To have more accuracy in our measurements a high resolution voltmeter (SOLARTRON-SCHLUMBERGER, 7061, 10 nV resolution), controlled by TestPoint[TM] via IEEE-488 interface, was used in our measurements. IEEE-488 norm offers very efficient functionalities to ensure that data are acquired by the controller as soon as possible and only if they are available: the Service Request (SRQ) and Serial Poll (SPL) procedures. More specifically, the voltmeter makes SRQ true when the measurement is available or if an error occurs. This ensures the synchronization of data acquisition: the controller waits for SRQ being activated before trying to read data. The controller sends Serial Poll to the voltmeter, which sends the value of the byte status. A logical mask (x and 64) checks if SRQ has been activated. A second logical mask (x and 88) checks if all is right (voltmeter ready and output available). If positive, data are entered, if negative (case of error), the voltmeter is reinitialized, the measurement is cancelled and a new measurement is launched.
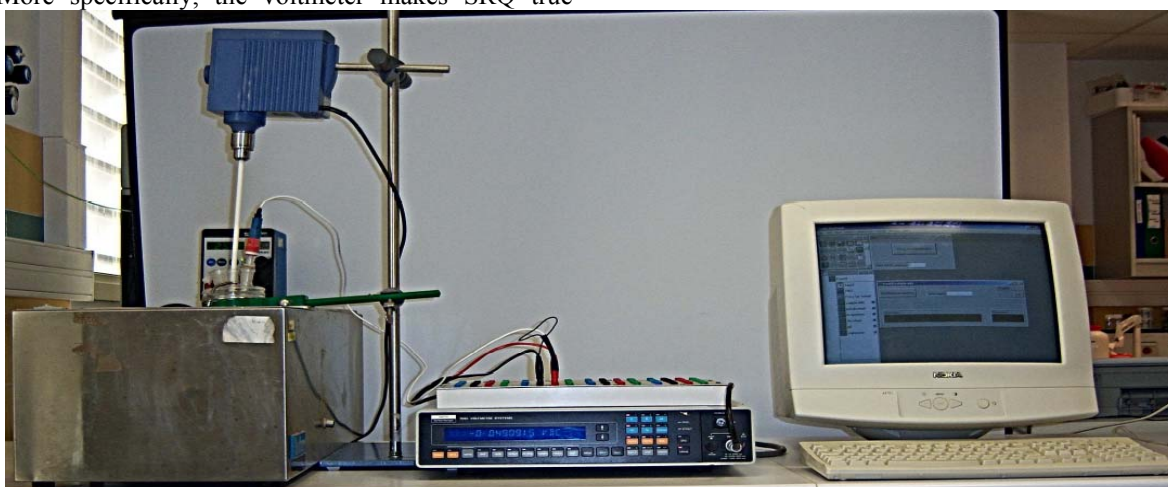

Fig. 5:   Presentation of equipment arrangements: computer containing TestPoint-CEC software and IEEE 488-interface, a high resolution voltmeter connected to pH electrode and computer and a standard solution placed in thermo-stated water bath with stirrer.
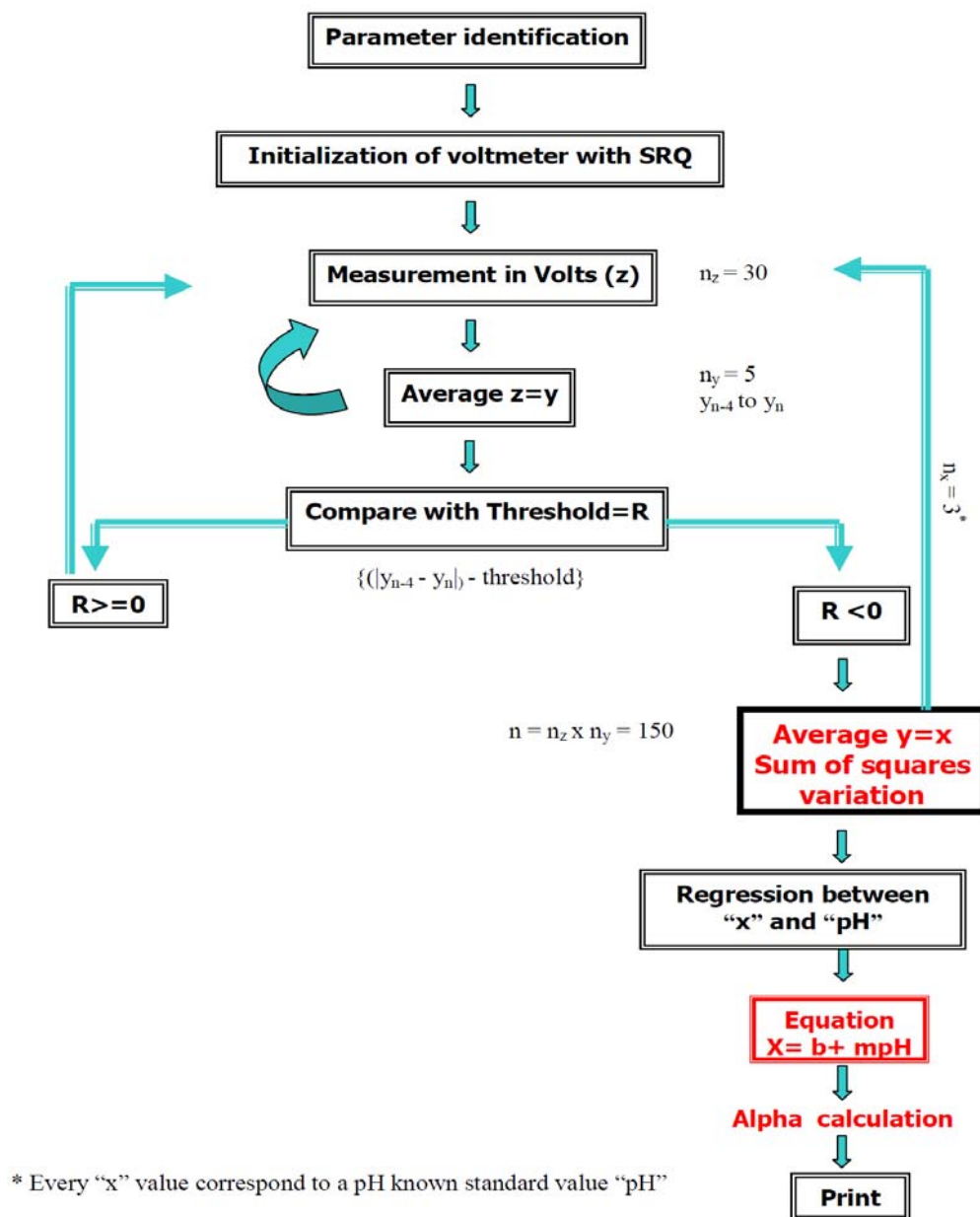
Fig. 6:   Flowchart of pH electrode verification and calibration program.

Sensor Verification Program

Flowchart of the pH electrode verification program (Fig. 6) represents the principle of the program and describes the statistic reliability of the results with an example. First step includes sample information which concerns the pH of standard buffer solutions, number of buffer solutions used to verify pH electrode, reference of pH combined electrodes or two separate electrodes and sample solution temperature. A file was already created in this program to store all the important information.

Second step consists of voltmeter initialization as program given in Fig. 2.D.

After initialization, measurement of solution in Volts and acquisition of data begins. Number of measurements n_z can be changed simply by increasing or decreasing the no. of loops in the program. For sake of simplicity of the example, we took 30 measurements as shown in Fig. 3. Average of z values, y is determined. Step of measurements and average is repeated five times and every time an average value y_i, from y_{n-4} to y_n is obtained. Variance

and sum of squares are also calculated in this program but here only average is discussed. Difference of average value y_{n-4} and average value y_n is compared to threshold value. Threshold value is set at the start of the program which is modifiable and depends on the reliability needed in results and the precision of standards. If answer R is equal or greater than zero, a new average value is obtained by the repetition of measurement and average steps which automatically eliminates the average value y_{n-4} at the same time. Now difference of average value y_{n-3} and newly obtained average value y_{n+1} is compared to threshold.

These steps are repeated again and again, comparing last five average values to threshold, until answer R is less than zero. This signifies that our pH electrode has attained equilibrium with the standard buffer solution. Once pH electrode is in equilibrium, average is calculated from all the values and x is obtained. As in this case, step of measurement n_z was repeated n_y times and each time taking 30 readings, so, x is the average of 150 readings. This value of x was then stored in the file.

Standard solutions were chosen according to IUPAC recommendations [13] and were thermostated at 25 °C (accuracy of 0.05) during measurements. We used three standard buffer solutions of pH 4.005, 6.857 and 9.182 respectively, for which the standard values are known with the maximum precision of 0.001 u.pH . The threshold chosen for convergence was 0.00025 V. We obtained a value x_i for each buffer solution. Regression was applied to calculate deviation of straight line from Nernst's law. This task would be easier in other programs, as TestPoint^{TM} is also compatible with Microsoft Excel. But compatibility of Microsoft Windows, Microsoft Office and TestPoint^{TM} is not same for all versions and future is still unpredictable. Additionally to operate our program independently we preferred to introduce the basic statistic formulas for regression in TestPoint^{TM} ourselves.

Conclusion

Graphical programming languages can be used to automate data acquisition. TestPoint^{TM} is based upon oriented object languages, but can be handled by scientists without a high level of specialization in software. TestPoint^{TM} makes it easy to timely verify a pH electrode. It does not cost much; we need only a computer, high resolution voltmeter, with interface GPIB and TestPoint. It takes less than 15 minutes to check the reliability of a pH electrode.

In this software package, the user also has a right to commercialize his programs. This type of program has been developed for the first time in TestPoint^{TM} environment and we think it could fulfil the basic requirements of pH measurements. It must be adapted to the specific language of command of the voltmeter. An IEEE-488 interfaced voltmeter, with Service Request (SRQ) functionalities is recommended. A basic knowledge of chemistry, statistics is of course useful. General experience in algorithmics is required if one wants to write his own programs. Using these calibrated pH electrodes with the insertion of digital burette in utilised equipments, automated alkalinity measurements (largely measured parameter in environmental chemistry) can also be carried out after just small modifications in the codes.

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