

TESTING, DETERMINATION AND VALIDATION OF THE MATHEMATICAL EQUATION AN ANTIMONY PH SENSOR

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Abstract: This paper presents testing mode, determining and validating the mathematical equation an antimony pH sensor. The introduction offers an incursion on the mine water and a definition of the pH concept, a brief history of it and continues with a short presentation of the elements which can make a possible variant of pH measurement, more precise the variant which use pH electrode/pH sensor. In the content of the paper is exposed a theoretical synthesis of the way of testing and validation of pH electrodes/pH sensors, which makes the transition to the actual testing of the studied pH sensor. The elements used for test and also the sensor response are viewed in photographs and graphics, which helps the reader to understand the practical part. Further, in paper, are presented short theoretical considerations followed by the dependence of electrical potential sensor analysis in relation with the change in pH solutions in which it was immersed. Conclusively, the most important conclusions are accentuated after the analysis, continued with some future research directions. Conclusions highlight the paper presented results, results that are seen as an opportunity for future studies.

Keywords: determination of pH ,pH electrode, test sensors, antimony, unifactorial linear regression ,analysis

1. INTRODUCTION

Mine water is meteoric water or groundwater composition undergoes changes due to interactions with mineral components of the deposit that you wash. Mine water is formed by mixing natural water from precipitation seeps into the mining and water network technology introduced in the process. Natural water seeps into the pores and cracks mine rocks by faults deposit or older works that are flooded, ruins, etc. drainage construction.

Work in quarries and underground mines expand, usually below the phreatic water layer and require controlled disposal of water that accumulates during mining operations.

Water flow is generally reduced if mining eruptive and metamorphic rocks excavated, and high or very high in the dug in sedimentary rocks, especially when they are unconsolidated, such as sand and gravel that are below Hydrostatic level.

In the mining water is needed to reduce dust in wet rock drilling operation for cooling compressors and other machinery, mineral processing, coal washing and hydrometallurgical extraction. For these applications, water is pumped from the surface water bodies and aquifers.

Streams that drain a surface mining area changes its composition by: quality and quantity of groundwater, storm water and waste water discharged into them. Sources of pollution of rivers where mining liquid waste waters are the results of extraction and processing the ore. Uncontrolled dumping, flow, drainage or untreated mine water infiltration into the environment causes the release of heat, suspended solids and dissolved chemicals, metals, metalloids, radioactive substances and salts.

Groundwater has a constant temperature of about 8 to 10 ° C, at a depth of 10 to 30 m should be kept in mind that underground mining usually reach depths exceeding 1000 m at these depths a factor in determining water temperature mine is geothermal gradient, increasing its value to depth of 1 ° C every 33 m.

The pH concept was introduced by Sorensen in 1909 as *pondus hydorgenii*, hydrogen exponent that become familiar to all chemists and biochemists specialists.

It is called the exponent of hydronium ion concentration or pH, logarithm with opposite sign of hydronium ion concentration from solution:

$$\text{pH} = - \lg c_{\text{H}^+} = \lg 1 / c_{\text{H}^+} \quad (1.1)$$

Later, when the thermodynamic significance of the notion of activity was better understood, the above definition was amended as follows:

$$\text{pH} = - \lg a_{\text{H}^+} \quad (1.2)$$

For diluted solutions, activities (a) are practically equal with concentrations (c). Therefore equation (1.1) is used more frequently, even if equation (1.2) is better founded theoretically.(reference [1])

Because a wide range of biological and chemical processes depend on pH, its measurement is one of the most common measurements made in laboratories.

Along with the introduction of the pH concept appeared and its measurements methods, therefore have appeared the glass electrodes, antimony electrodes, quinhydrone electrodes, etc. used for pH measurement.

In process of time for easing the performing measurements, on the market appeared the combined pH electrode (its schematic presentation can be found in reference [2]), having as constructional elements indicator and reference electrodes.

As described in reference [3] and presented below, a sensor is defined as a device that receives a stimulus and responds with an electrical signal. The stimulus is the quantity, property, or condition that is sensed and converted into electrical signal.

A sensor is a translator of a generally nonelectrical value into an electrical value. Hereunder when talking about electrical values, means a signal that can be channeled, amplified and modified by electronic devices. Therefore, the combined electrode can be named sensors, because in the same time with his immersion in aqueous solutions responds with an electrical signal.

2. THEORETICAL CONSIDERATIONS ON TESTING AND VALIDATION OF THE PH ELECTRODES/PH SENSORS

In reference [4], the antimony electrode performance on the pH sensitivity was evaluated by measuring the open circuit potential (OCP) in pair with a commercial reference electrode Ag/AgCl saturated, in aqueous solutions buffers. OCP can be measured by a laboratory pH/mV-meter or a digital multimeter with a data acquisition device connected to a computer.

In order to observe the calibration curve of tested electrodes, it has been made an acid-base titration for changing the pH in the test solution. A multi-ion universal buffer solution with the composition of 0,01 M H₃PO₄-H₃BO₃-CH₃COOH and 0,1 M KCl was prepared as the base solution, its initial pH was about 2.

After both the Sb/SbO_x electrode and the Ag/AgCl reference electrode were immersed into the test buffer solution and the OCP reading became stable, 0.1 M KOH solution was added step by step and the electrode potential difference would change correspondingly.

The solution was stirred magnetically throughout the measurement and a previously calibrated glass pH electrode was used to monitor pH of the solution at the same time.

Sometimes two or more electrodes sharing a same Ag/AgCl reference electrode were inserted into the test solution together for the measurement, to check the reproducibility for the fabrication of the electrodes.

3. TESTING OF ANTIMONY PH SENSOR

In the case of the antimony sensor (whose construction is presented in the document [5]), for testing it under the similar conditions to its application environments, it has been used approximately the same procedure described in reference [4] and presented previously in a synthesized manner. As we can see in Fig. 1, the elements used for performing measurements are: the heated magnetic stirrer, pH – meter, a temperature probe, pH glass sensor and of course, the antimony sensor. Exception to those presented in the theoretical considerations, is that the measurements was prepared a mixture of phosphoric acid, acetic and boric with concentration of 0.04 M each, and for obtaining the buffer solution with desired pH value was added at 100 ml of mixture solution, X-ml of a 0,2 n NaOH. [6]

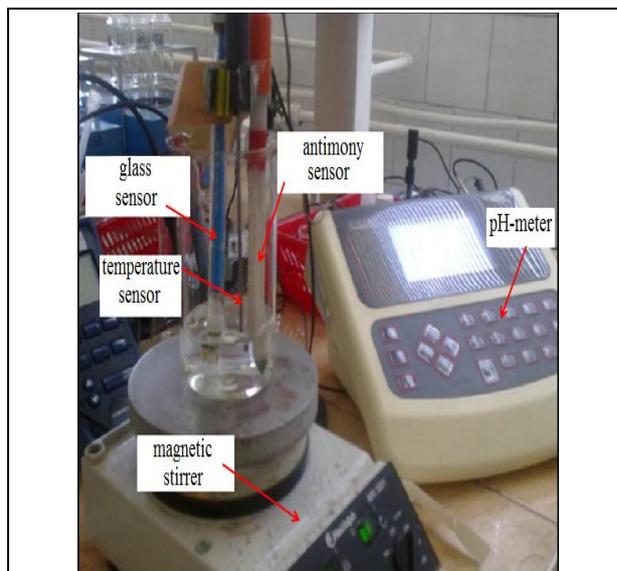


Fig. 1. Items used for measurement process

The sensitive performances of the antimony sensor, determined according with the above presentation occurs in a graphical form in Fig. 2. We can affirm that in the range of pH 2-10, the sensor has a fast and stable response to pH changes in aqueous solutions. Its potential has a linear relation with the pH of solutions (coefficient of determination $R^2=0.9997$) and a slope of 50.95 mV/pH. Sensor response time was between 7 and 25 seconds, being determined empirically.

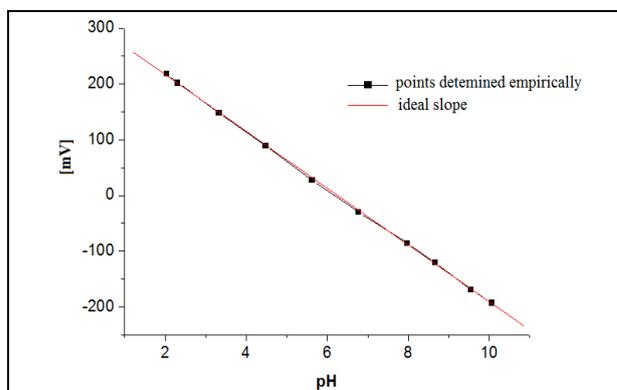


Fig. 2 Response of antimony sensor on pH range 2 to 10

In case of soil monitoring has sought an alternative to glass sensor, due to its membrane fragility. So, we focused our attention on metal / metal-oxide electrodes, and more precisely, on the antimony pH electrodes. The choice of this type of electrode was not random, being grateful to a relatively large number of scientific papers, reference [8] etc., that presents the antimony electrodes as one of the best alternative for monitoring the pH of soils. Therefore, after a study on the existent literature in this domain, it was developed a sensor adapted to laboratory monitoring of soils, whose construction is shown in reference [11]. The measurements made with the sensor, and the measurements made with other types of sensors, are based on the relation between electric potential response resulted after their immersion in buffer solutions with different pH value (pH buffer solutions ranging between 2 - 10).

4. THEORETICAL CONSIDERATIONS REGARDING THE CONNECTION BETWEEN RESPONSE ELECTRIC POTENTIAL OF SENSOR AND THE BUFFER SOLUTIONS

The first issue which must be resolved in the analysis of connection between a dependent variable (the result, effect, explained, denoted by Y) and one or more independent variables (factorial, causal, explanatory, denoted by X_i) refers to the question: is there a connection between variable, or changing the effect-variable is influenced by causal-variable (variables) changes? For answering at this question requires to start from theory and respectively from specialized science which studying these phenomena and from empirical data recorded for the variables assumed to be correlated. Through regression method it can be analyzed through an analytical expression, called regression function, the manner of behaving the dependent variable Y in relation to the modification of one or more independent variables (X_i).

Regression function expresses, in average the behaving of effect-variable, under influence of one or more effect-variables, in conditions where all other causal-variables, essential or accidental, would exert a constant action or would exert a non-essential influence.

Regression function is a mathematical function that expresses the relation between variables and has the general form:

$$Y_{xi} = f(x_1, x_2, \dots, x_k) + e \quad (4.1)$$

where "e" is the random disturbance variable or error value, that summarizes all factors not taken into account, unspecified.

If the regression involves one independent variable, it will be applied the linear or non-linear regression, and if the dependence of variable Y will acyclizate in function by at least two factorial variables, it will be applies the multifactorial regression.

Choosing the regression function can be a simple thing, based on graphical representation of pairs of values $x_i y_i$ (reference [7]).

5. DEPENDENCE OF ELECTRICAL POTENTIAL SENSOR ANALYSIS IN RELATION WITH THE CHANGE OF SOLUTIONS PH IN WHICH IT WAS IMMERSSED

Currently there is a wide range of commercial software on market, using the statistical calculus, exemplifying : EXCEL, MATLAB, STATISTICA, MINITAB, DESIGN EXPERT, etc. The link between potential response of the built sensor (voltage supplied to it), E, and the solutions pH that has been immersed for the measurements, pH, can be written in a general mathematical form as:

$$E = f(\text{pH}) \quad (5.1)$$

To establish this relation were taken into account the results of testing the sensor in buffer solutions that were obtained as follows:

It was prepared a mixture of phosphoric acid, acetic and boric with concentration of 0.04 M each, and for obtaining the buffer solution with desired pH, was added to 100 ml mixture, X-ml indicated by 0.2 n NaOH. Therefore, the graphical representation of the solutions pH and the potential responses of the sensor made is presented in Fig. 3.

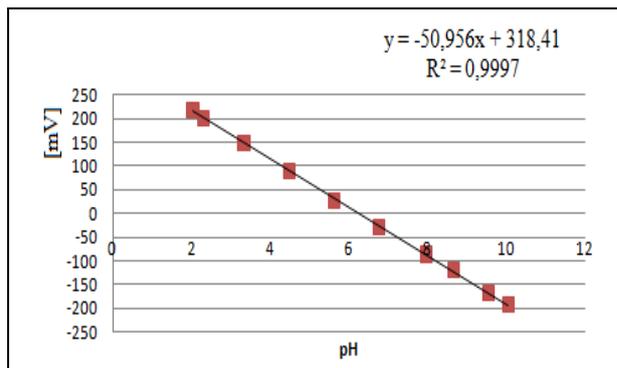


Fig. 3. The graphical representation of the solutions pH and the potential responses of the sensor

Introducing the Excel data obtained from the test of the sensor and again appealing to the specialized computer package, wherefrom, after selecting the main menu options <Tools>+<Data Analysis> + <Regression>, it will obtain these results, see Tab. 1. :

SUMMARY OUTPUT	
<i>Regression Statistics</i>	
Multiple R	0,99985431
R Square	0,99970864
Adjusted R Square	0,999672221
Standard Error	2,743378037
Observations	10

Tab. 1. Summary output

Multiple R represents the correlation ratio (R), whereby it measure the intensity of the relation between the solutions pH and the of electrode potential. R = 0.9998 shows that between pH solutions and the potential response of the electrode is a strong connection.

The coefficient of determination ($R \text{ square} = R^2$) has the value 0.9997, which means that the regression model explains 99.97% of the variation of sensor's potential response. It is also computed the adjusted coefficient of determination, which is usually used in multiple regression. It is calculated the standard error , equal to 2.7433. If this value was zero, it could be said that all points are on the right side of the regression.

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95,0%	Upper 95,0%
Intercept	318,411458	2,061390702	154,46439	3,45197E-15	313,6578824	323,165033	313,6578824	323,1650334
pH(x)	-50,955832	0,307557844	-165,67886	1,97072E-15	-51,66506155	-50,2466022	-51,6650616	-50,24660224

Tab. 2. Regression coefficients calculus

Tab. 2 represents regression model coefficients, intercept - constant term (318.4114) which is where the regression intersects the y axis (the value of y when x = 0), and coefficient b is -50.9558, which means that increasing the pH by one unit, the number mV's drops with 50.9558.

Hereunder we test the significance of these coefficients, with the „t” test, because $t_{b0} = 154.4643$, and the threshold of significance P-value is $3.452 \text{ E-}15 < 0.05$ means that this coefficient is *significant*.

Regression equation is: $y = 50,956 x + 318.41$.

The model reflects the link between pH of the solutions and the voltage supplied by the sensor, validity of the model is tested using the "F" test (Fischer - Dispersion analysis ANOVA), see Tab. 3.

ANOVA	df	SS	MS	F	Significance F
Regression	1	206588,191	206588,191	27449,4836	1,9707E-15
Residual	8	60,20898444	7,526123055		
Total	9	206648,4			

Tab. 3. ANOVA Tab

df - "the degrees of freedom"

SS - "the sum of squares"

MS - is the ANOVA expression of variance, or, "the mean squares"

F = MS (factor) / MS (error) - is the ratio ANOVA

The ANOVA Tab. represents the calculus of three variances: the model explained, residual and total. With those it is calculated $F = 27449.4836$. Significance F (significance threshold) is $1.97072 \text{ E-}15$ (value less than 0.05), resulting that the built regression model is valid and can be used to analyze the dependence between those two variables.

6. CONCLUSIONS

The antimony sensor adapted to a laboratory installation used for the monitoring the soil, has a sTab. response to pH changes in aqueous solutions. Its potential has a linear relation with solutions pH (coefficient of determination $R^2 = 0.9997$) and a slope of 50.95 mV/pH.

Because the obtained results in terms of performance sensitive sensor were satisfying, studies will continue to reduce the dimension of the sensor and to improve its functional performance.

After studies and tests of the antimony sensor, we can say that the sensor can be successfully used in practice. It shows a linear and sTab. response to pH changes in range 2-10. Its response time is relatively fast, and it was empirically determined in several series of tests. As a

future goal, it follows the testing of this type of sensor on several soils, whether polluted or not, under either laboratory facilities or in open environments.

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