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DESIGN AND EXECUTION OF AN ANTIMONY SENSOR USED FOR MONITORING OF SOIL pH

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Abstract

The current paper presents the method that designs, manufactures and tests antimony based pH sensor used for monitoring of soil pH. In the first stage of this work the method of manufacturing the sensitive antimony elements is presented. These sensitive elements are casted into different forms (conical and cylindrical). These are subjected to a series of analysis in order to determine the chemical composition of the material used 99.73% Sb, 0.27% Ti (EDX), the morphology of the structure (SEM) and the characteristics of the oxide layer (XRD). The second part of this paper explains the method of testing the manufactured antimony sensors in the reference pH solutions. Finally, the sensors are used for measurements and are tested, alternatively, in pairs, with a reference Ag/AgCl sensors found in commerce. The results of these measurements show values approximately identical at both manufactured sensors. The adapted sensor that was obtained shows a relatively fast and stable response to pH changes in aqueous solutions. Its potential has a linear relation with pH solutions and a slope of 50.95 mV/pH.

Key words:*antimony, monitoring, pH, sensor, soil.*

INTRODUCTION

The pH of the soil is one of the most used indicators in order to observe and to analyse the processes that are taking place into the soil. The monitoring of soil' pH is done when different type of analyses are required to be done in the soil, or during a certain treatment process, in order to observe the variations (Matei et al., 2011; Predescu et al., 2017).

When making a monitoring of the soil pH, one of the most important things is the pH sensor (Hayat et al., 2014). Due to the fact that not all sensors found on the market are adequate, it is necessary to adapt some of them.

The most used sensors for pH measurements are the ones with glass membrane (Norman et al., 2000), but they are difficult to miniaturize, have mechanical fragility and chemical instability in corrosive systems. Studying the scientific literature we can observe that potentiometric metal oxide electrodes, specifically antimony electrodes, are common in soil pH measurements (Schirrman et al., 2011).

For ease of experimental measurements in a laboratory model, a pH sensor was built with indicator electrode and comparison electrode of the same material, antimony. The use of a pair of electrodes of the same material for the construction of pH sensors was presented by Jovanović et al., (1969) in their paper.

pH is one of the most commonly used indicators to have an overview of the processes occurring in the soil. Several methods for the characterization of soil pH were described by Thomas et al., (1996). Some researchers have focused on water pores from the soil and they used wells or piezometers for waterlogged soils or suction samplers that allow sampling water from soil pores (Elberling et al., 2007).

Currently, commercial glass electrode is the most used for measuring the pH, due to reliability and comfort of the measurements performed with it. In addition to the general requirements, including rapid response, high sensitivity, long term stability, and ensuring reproducibility of pH measurements, the pH electrode should be easy to be manufactured in a proper shape and size without losing its mechanical strength [da Silva et al., 2008; Ha and Wang, 2006).

The glass sensor disadvantages focused our attention to metal-metal oxide electrodes, a study that was presented in Stoica and Micle, 2011. Many bibliographic sources present the usage of antimony sensor to measure soil pH between plant roots (Baghdady and Sommer, 1987), for mapping soil pH (Schirrman et al., 2011), or in other areas, for measuring dental plaque pH (Ro et al., 2008), for continuous potentiometric determinations of acetic acid from vinegar (Capelato et al., 1996). This shows that on-line monitoring of pH using antimony electrodes is proved to be a success.

Luca (1973) presents an electrode manufacturing as simple casting in the desired shapes or by molten antimony being absorbed into a glass capillary tube – „the method of the capillary absorbed smelt”.

Sheng et al. (2013) demonstrated in their experiments that the double membrane modified antimony pH electrode testing instrument would be suitable for *in situ* and continuous pH measurement in many applications.

Boyes (2003) showed that the antimony electrode is a simple piece of pure antimony rod (~12 mm diameter, 140 mm length), placed in a plastic body with a protective role, which is resistant to acids attack. When immersed in a solution containing dissolved oxygen, the antimony rod prominence will be covered with antimony trioxide - Sb_2O_3.

For the execution of the electrode, antimony was strongly heated in a crucible until melted. The smelt was casted in a thin glass tube where it was left for solidification, thus obtaining a metal (antimony) rod with internal dimensions of the tube (Caflisch et al., 1978).

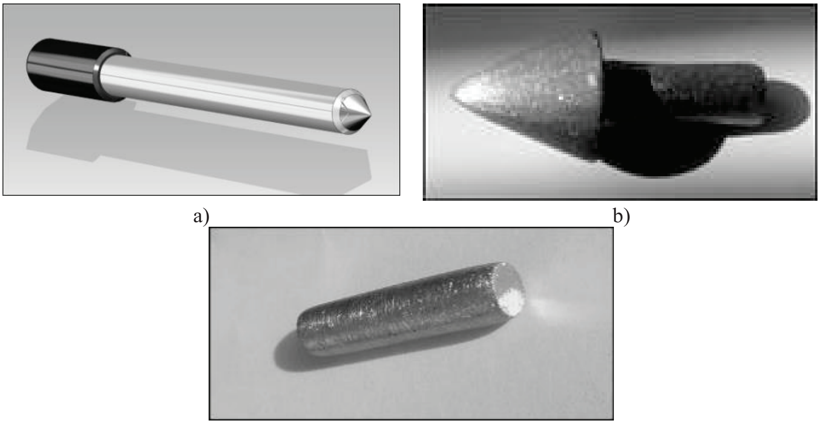
In his study, Luca (1973) was schematically showing the construction of an antimony electrode consisting of a cast rod of antimony, fixed in a hard rubber, glass or plastic body with an epoxy resin, a wire being attached as a connection element. Since no special precautions are taken, the metal electrode surface is covered, in moist air or in aqueous solutions with a thin film of antimony trioxide.

The aim of this paper is the design, execution and testing of antimony manufactured pH sensor used in soil monitoring.

EXPERIMENTAL

Construction of the sensors

The sensitive elements of the pH sensor such as the measure and reference sensors head were realised by melting antimony in a crucible at the temperature of 750°C and casting in moulds, in order to obtain a pH sensor (Figure 1a). The heads were adjusted to the desired dimensions and two sensitive antimony elements were obtained:



a) b) c)

Figure 1. Antimony pH sensor design and sensitive elements executed:
a) designed version of the antimony pH sensor; b) conical sensitive element;
c) cylindrical sensitive element

1. ***conical*** shape element (Figure 1b) with the total length of 15 mm (from which 10 mm is the length of the conical part), the diameter of the conical part of 10 mm and the diameter of cylindrical part of 4 mm;
2. ***cylindrical*** shape element (Figure 1c) with a diameter of 2 mm and a length of 10 mm.

The sensitive elements are assembled in order to obtain a pH sensor which can be used to monitor the soil pH. The two elements are introduced into a body made of plastic and glass.

Characterization of the sensitive elements

The sensitive elements were analyzed by: Energy dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM) in order to determine the morphology of the structure of the sensitive element and X-ray diffraction (XRD) for the characterization of the oxide thin layer on the surface of the sensitive element.

Testing of the manufactured electrodes

The manufactured electrodes were subjected to a series of measurements in acid and alkaline medium (reference pH buffered solutions) purchased from commerce. Using a reference electrode Ag/AgCl which exists on the market, in pair with the electrodes manufactured, we obtain comparable measurements with all antimony electrodes existing on the market.

Testing of the manufactured sensor

The manufactured sensor was subjected to a series of measurements in acid and alkaline medium (pH 2 to 10) - reference pH buffered solutions. For measurements, it was prepared in the laboratory a mix of phosphoric acid, acetic and boric, each of them in concentration 0.04 M. For obtaining of buffering solution with desired pH, there was added at 100 ml of mixing X-ml indicated solution NaOH 0.2 n (Lurie, 1970).

All measurements of tested antimony sensor were compared with a glass sensor commercially available.

For the last test measurements, the antimony sensor and the commercial glass sensor were put in buffering solution commercially available.

RESULTS AND DISCUSSIONS

Construction of the sensor

The main components of antimony pH sensor are: antimony element head (the sensitive H+ part), plastic body, reference electrode with antimony head and glass body (positioned inside of plastic body), ceramic junction which makes contact with medium, metallic conductors (realized from electrical contacts), plastic cover and cable for connection.

If the components (head, body, metallic conductors, and cable for connection) are assembled in order, we can obtain pH electrodes: in this case, conical and cylindrical shape. The conical sensitive element was equipped with a plastic body and the cylindrical one with a glass body.

The plastic body has a length of 140 mm, outside diameter of 14 mm and 12 mm interior diameter - in this form, it can be used as electrode body. It is threaded on one end and drilled in two places, resulting in a slot that can be used for filling with electrolyte and a slot in which the ceramic junction was mounted - in this form it can be used as body sensor. The pH sensor produced (Figure 2) has a length of 180 mm (without considering the cable), out of which the length has 40 mm and the cover has 16 mm – with the possibility of 10 mm threading on the plastic body.

The glass body has a length of 50 mm and a diameter of 2 mm. The cylindrical shaped sensitive element has on one end tinned a copper metallic conductor which is continued within the cable, then the subassembly is introduced in the glass body and the other end is sealed with an epoxy resin (Figure 3).

To obtain a sensor, the metallic conductor elements of each electrode were connected to a cable and then protected with the plastic cover.

Characterization of the sensitive elements

The chemical analysis (EDX) of the sensitive element (Figure 4) consists of 99.73% antimony (Sb) and 0.27% titanium (Ti).

The nested nature of metallic antimony (Figure 5) existing under an oxide layer grown on the surface of the sensing element can easily be observed by the scanning electron microscope (SEM).

In a cross-section (Figure 6) through the sensitive element, it can be observed the thickness of the oxide layer. Metal surface (B) is covered with porous oxide layer (A) which protects the metal.

In order to determine the crystalline phase of the oxide, powder was taken from the electrode surface and it was examined using X-ray diffraction (XRD).

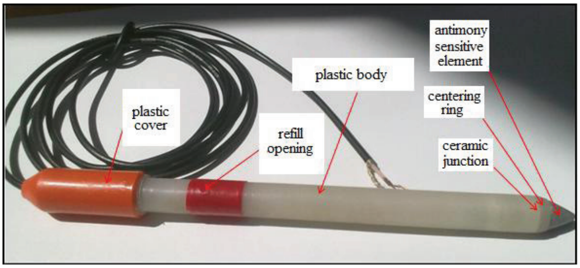


Figure 2. Plastic body antimony conical element

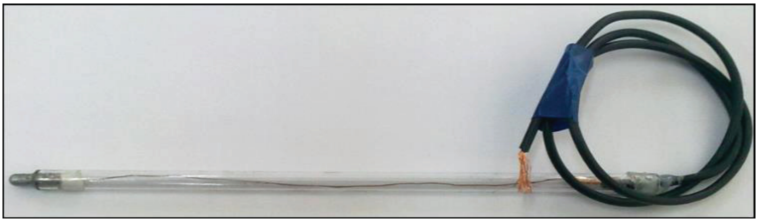
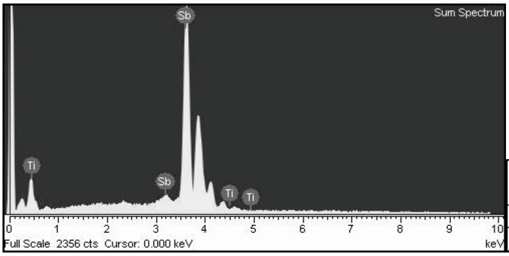


Figure 3. Glass body antimony cylindrical element



Element	Weight %	Atomic %
Ti	0,27	0,69
Sb	99,73	99,31

Figure 4. Chemical analysis of the sensitive element

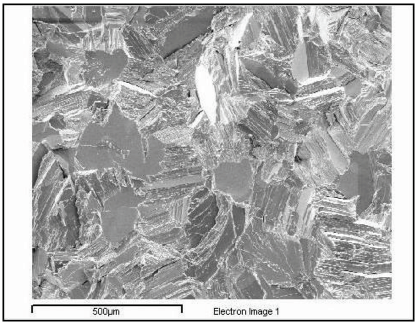


Figure 5. The morphology of the casted sensitive antimony element (SEM)

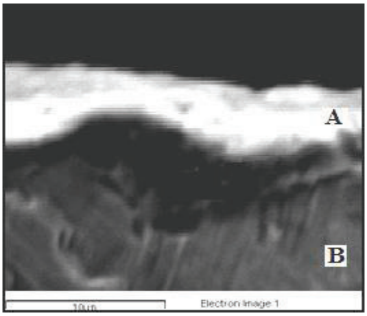


Figure 6. Section through the sensitive element observed using SEM: A) oxide layer; B) antimony metal

Peaks, identified in the Figure 7, match the pattern combination Sb_2O_3 and the Sb metal. The existence of Sb metal can be attributed to the fact that at the time of sampling (by scraping) for XRD, the very thin oxide layer of the metal was also sampled with it.

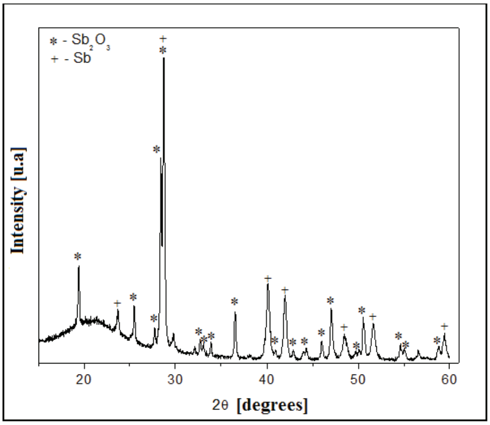


Figure 7. XRD result of antimony oxide powder scraped from the oxidized element surface

Testing of the manufactured electrodes in similar applicability medium conditions

Manufactured electrodes were tested in acidic and alkaline mediums which were established using pH standard solutions existing on the market in working temperature of 25°C. The potentials were measured by a mili-voltmeter of high precision ± 0.01 mV. Constant temperature of 25°C was maintained with help of circulated heated bay device.

Operational characteristics of antimony electrodes with plastic and glass body were established in standard pH solutions, in the range of 2 – 10. For these tests, it was used a commercial Ag/AgCl reference electrode, in pair with each laboratory-made electrode.

The electrodes response is presented in Figure 8. Both sensors presented a stable and rapid response to pH changes in different aqueous solutions. There is not a big response difference between antimony sensors and commerce glass ones. Potentials of antimony electrodes present a linearity relationship with the solution pH in which they were immersed. The determination coefficient was R^2=0.9972 for plastic body sensor, R^2=0.9969 for glass body sensors and sensitivity was 47.95 mV/pH, respectively 48.60 mV/pH.

As a result of multiple trials, the following functional characteristics were established:

- Operational linear domain: 2 - 10;
- Temperature range: 10 - 60 °C;
- Sensitivity: 50 ± 3 mV/pH;
- Frequency: ± 3 mV;
- Precision: 0.1 pH;
- Response time: less than 60 seconds;
- Fiability: high.

The disadvantage of using electrodes with antimony measurement sensitive element in pair with Ag/AgCl reference is the fact that for direct reading of the pH, special pH-meters are needed, different from those used in measuring the pH with glass sensor.

The glass sensors manage to compensate an asymmetry of potential of approximately -370 mV. Using a pair of sensors of antimony measuring element and antimony reference sensors proved to be the solution to eliminate this inconvenient. This fact is proved in the following experiment, where were used: the two manufactured electrodes (measurement electrodes: one with conical sensitive element (Figure 2) and one with cylindrical sensitive element (Figure 3), a manufactured antimony reference electrode – cylindrical shape (having a KCl solution as electrolyte) and an Ag/AgCl reference electrode (purchased from commerce).

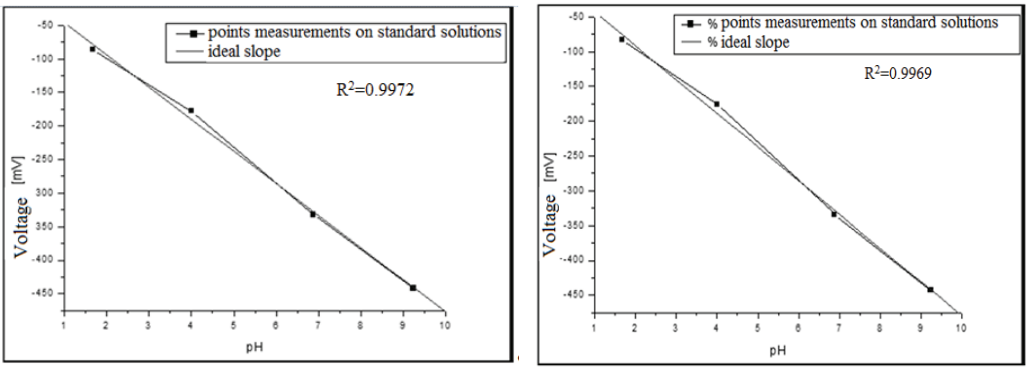
Analyzing the results presented in Table 1, it can be seen that there were obtained values almost identical for both sensors used. The results of the tests show that in the case of using antimony electrode with antimony reference, it is no longer necessary to use a special pH-meter to compensate the asymmetry of potential.

Testing of the manufactured sensors in similar applicability medium conditions

The antimony sensitive sensor's performances are presented in Figure 9 for the pH interval from 2 to 10.

It has a relatively fast and stable response to changes in pH in aqueous solutions. Its potential has a linear relationship with solutions pH (determination coefficient R^2=0.9997) and sensibility of 50.95 mV/pH.

The time for one performed measurement of the sensor is between 7 and 25 seconds.



a) b)

Figure 8. Response curve for electrode at 25°C: a) plastic body; b) glass body

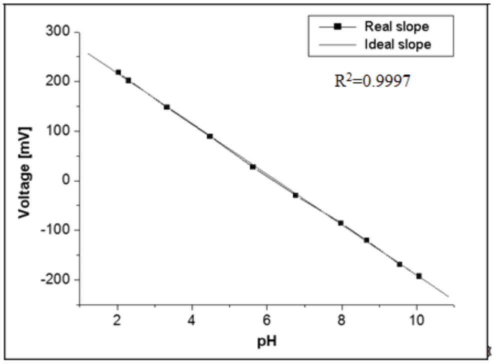


Figure 9. Antimony sensor response on pH range 2 to 10

Table 1. Comparison between measurements performed by indicator antimony sensors and indicator Ag/AgCl sensors

Open circuit potential obtained using measurement electrode and E_{RefSb}/ E_{Ref}	*pH*	6.88	4.01	9.23	ΔE
Plastic body – conical Sb element and E_{RefSb}	***Sb / E_{RefSb}[mV]***	-26	+138	-127	265
Plastic body – conical Sb element and E_{Ref}	***Sb / E_{Ref}[mV]***	-329	-168	-435	267
Glass body – cylindrical Sb element and E_{RefSb}	***Sb / E_{RefSb}[mV]***	-25	+143	-124	267
Glass body – cylindrical Sb element and E_{Ref}	***Sb / E_{Ref}[mV]***	-329	-170	-436	266

Note: E_{RefSb} –Sb reference sensor
E_{Ref} - Ag/AgCl reference sensor

CONCLUSIONS

The functionality of the manufactured sensor was proved by verifying the accuracy of the information acquired by a number of other sensors and other equipment purchased commercially.

The antimony sensor shows a linear response in 2 - 10 pH intervals, being resistant from mechanical point of view and can be used in corrosive medium which contains hydrofluoric acid.

The responses of the manufactured sensor were compared with the responses of a glass pH sensor. The experiments demonstrated that the manufactured sensor measurements were correct, with an error of ± 0.2 pH units.

The drawback of using pH meters of a special construction was removed by using in the construction of the sensor a pair made of antimony, indicator and comparison.

The difference between this sensor in comparison with other types of sensors existing on the market is related to the shape of the element head that can be easily inserted into the soil.

The antimony sensor manufactured is showing a relatively fast response and stable to the pH changes in aqueous solutions. Its potential has a linear relation with the solutions' pH (determination coefficient R^2=0.9997) and a slope of 50.95 mV/pH.

It can also be seen that the shape and dimensions of the sensitive elements do not influence the measurements.

As a result of designing, manufacturing and testing the pH sensors, we can conclude that the manufactured sensor presented in this paper can be successfully put into practice.

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