

# FUZZY- SYMBOLIC ION ACTIVITY MEASUREMENT IN TEST SOLUTIONS

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**Abstract** - This paper deals with several possible variants of selective electrodes used for measuring the concentration of ions that exist in test solutions. It presents the basic principles of the method, the possibilities of expanding it with a view to obtaining useful collateral information. Finally, a fuzzy-symbolic ion activity measurement and the configuration of a multi-sensor, computer piloted measuring system, capable of offering such information is presented.

**Keywords** - ion activity, selective electrodes, fuzzy-symbolic sensors, multi-sensor system.

## 1. INTRODUCTION

The measurement of the activity of hydrogen ions in aqueous solutions by means of glass electrodes has been investigated for many years now. Starting with 1960 another issue has been put forward that of evaluating the activity of other ions that exist in biological media.

The glass electrode it self acquired special compositions of these studies has been the identification of the selectivity of various materials that are electroactive to certain ions [1].

Chemical sensors differ significantly from physical sensors because of the great number of chemical parameters. As examples, the number of ions in the human blood is so large that selectivity or specificity becomes a crucial property of chemical sensors [2].

The ion selective electrode is widely used in a large variety of application in research, industrial processing and clinical analyses [3].

In the Recovery Hospitals of Iassy-Romania, the application of ion selective electrodes includes the determination of ions in blood, urine and sweat [4]. Because the number of analyses is high, and most of such analyses are in normal limits, a method for discriminate the test solutions with bed results is necessary.

This paper describes a fuzzy-symbolic method for ion activity measurement and the configuration of a multi-sensor computer piloted measuring system, capable of offering this result and other useful collateral information. This method can be used also for on-line control in industrial applications,

medical monitoring, and reliable fire alarms, optimising the performance of car engines.

## 2. SELECTIVE ELECTRODES

The membrane represents the essential element of selective electrodes. The material it incorporates gives its selectivity. For example, the potassium selective electrode (Fig.1) has an antibiotic (valinomycin) in the structure of its membrane [4]. The dimension of the internal cavities belonging to this structure allows only the penetration of ions whose radius is not longer than of potassium ions ( $K^+$ ). This way, such a membrane becomes selective only for potassium. If this electrode gets into contact with a fluid biological medium (e.g. a serum), the  $K^+$  ions permeate the membrane, leaving behind the chlorine ions with a negative charge  $Cl^-$ , which thus form a negative line under the positively-charged membrane.

In a state of equilibrium, the membrane potential is proportional to the activity of the potassium  $K^+$  ions. In an ion selective electrode, the reaction is produced within its membrane and does not consist in a transfer of potassium ions between the solution to be tested and that of the electrode.

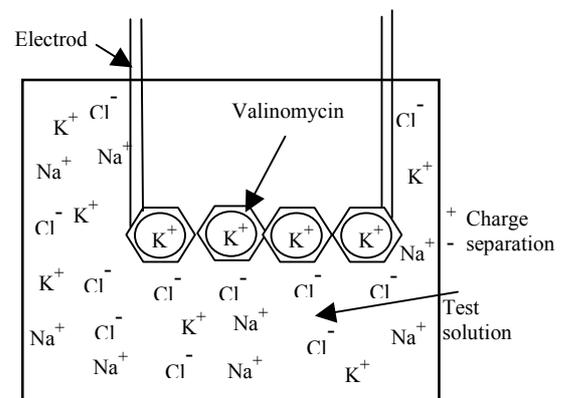


Fig.1 – The potassium selective electrode

A system made up of two electrodes is used to measure the membrane potential; one has a membrane sensitive to a

certain ion and the other one-the reference electrode- offers the potential of a known solution (Fig. 2).

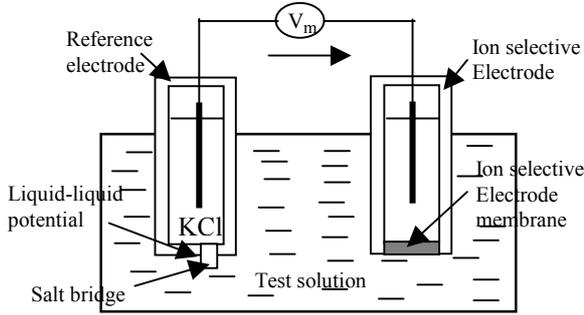


Fig.2 - Measurement circuit with selective electrode.

In this case, the interface potential depends on the activity of the ions under discussion present in the solution to be tested and in the reference solution. If  $a_1$ ,  $a_2$ , are the activities of the ions in the solution to be tested and in the reference solution, the overall potential of the membrane is given by Nernst's equation:

$$V_m = \frac{R \cdot T}{n \cdot F} \ln \frac{a_1}{a_2} \quad (1)$$

where  $n$  represents the number of the ion's units quantity of electricity,  $R$  is the universal gas constant,  $T$  is the temperature in Kelvin (degree) and  $F$  is Faraday's constant. If  $a_2$  is constant (the activity of the reference solution), the membrane potential will be:

$$V_m = V_0 \pm \frac{R \cdot T}{n \cdot F} \ln a_1 \quad (2)$$

where  $V_0$  is a constant depending on the system of electrodes.

In order to make it possible for this potential to be measured electronically, the reference electrode is introduced in the solution under study by means of a so-called salt bridge. Also, some variants replace the internal reference solution which a direct metallic contact, or an encapsulated one. Recent studies impose different variants of electrodes of the integrated type. A typical ISFET structure is presented in Fig. 3.

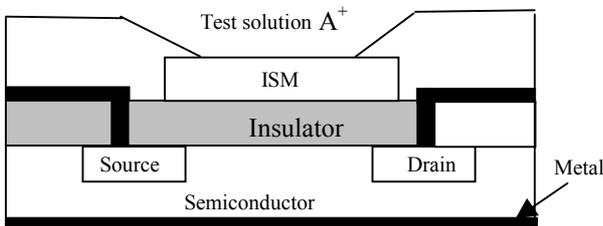
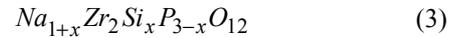


Fig.3 - Typical ISFET selective structure.

The ion-selective material ISM is deposited directly on the ISFET gate. Depending on the type of materials and the distribution of loads in its volume, the sensor's response follows a Nernstean law or a non-Nernstean law.

The membrane of the sodium sensor is based on a Na super ionic conductor pellet. It is a ceramic material with the following chemical formula:



It has been shown that the ionic conductivity is a function of the sodium stoichiometry ( $x$ ) of the material. The best conductivity has been obtained for the composition  $x$  about 2 or 2.2. At room temperature, the conductivity is about  $10^{-3} \text{ S.cm}^{-1}$ , which is extraordinarily high compared to that of usual sensitive membranes (lower than  $10^{-6} \text{ S.cm}^{-1}$ ). Several ways can be used to elaborate the Na super ionic conductor samples. The advantages of sol-gel routes have been shown to synthesize the Na super ionic conductor powders for  $Na^+$  sensors. Such a chemical process is based on hydrolysis and condensation reaction of alkoxides with an excess of water. Very fine powders can be obtained in this way and so the sintering temperature can be lowered 1200 to 1000 °C. to avoid a loss of Na and P, which are volatile elements. The dried powder is then prepressed in a double-punch disc and finally pressed isostatically at about 250 MPa [5].

Na super ionic conductor pellets can be assembled with an internal reference solution, and the waterproof is provided by a joint or by sealing with epoxy resin (Fig. 4), or with solid state internal reference systems, allowing the use of small pellets of Na super ionic conductor (Fig.5).

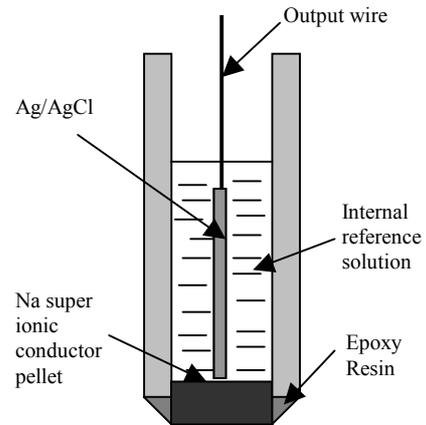


Fig.4 – Ion selective electrode with liquid reference

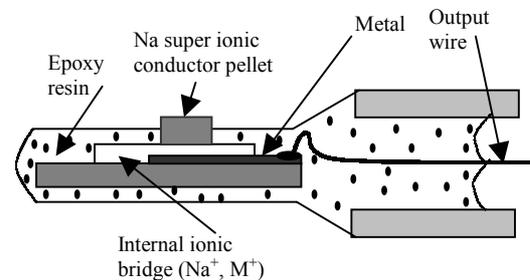


Fig.5 - Ion selective electrode with solid state internal reference

Ion selective electrodes often exhibit a response to other ions.

The response of the selective electrode in the presence of an interfering  $j$  is given by the Nikolskii-Eisenman equation:

$$V_m = A + \frac{k \cdot T}{z_i \cdot e} \ln(a_i + K_{ij} a_j^{z_i/z_j}) \quad (4)$$

where  $V_m$  is the electrode voltage response to the primary ion  $i$  in the presence of the interfering ion  $j$ .  $k$ ,  $T$ , and  $e$  are, respectively, the Boltzman's constant, the absolute temperature, and the elementary charge,  $z_i$  and  $z_j$  are respectively the charge of the primary and interfering ion,  $a_i$  and  $a_j$  are respectively the activity of ion  $i$  and  $j$ ,  $K_{ij}$  is a quantitative measure of the electrode ability to discriminate the interfering ion referred to as the selectivity coefficient, and  $A$  is a material constant. The activity of an ion  $i$  in test solution is related to its concentration  $c_i$  by the equation:

$$a_i = a_{ci} \cdot c_i \quad (5)$$

where  $a_{ci}$  is the activity coefficient, which depends on the types of ions present and on the total ionic strength of the solution.

### 3. FUZZY-SYMBOLIC ION ACTIVITY MEASUREMENT

To perform symbolic ion activity measurement, it is necessary to specify the relations between symbols and numbers. Let  $S$  be the set of symbols and  $A$  the set of all ion activity measurements. The meaning of a symbolic value is called a *translation*  $t$  and is defined as an injective application from the set of symbols associated to this universe  $S(M)$  and the set of subsets of  $S$ ,  $P(M)$  [6]:

$$t : S(A) \rightarrow P(A) \quad (6)$$

The symbolic ion activity measurement is obtained by means of a new application called a *description*  $d$ , which associates any activity measurement to a subset of the symbolic set  $S(A)$ :

$$d : A \rightarrow P(S(A)) \quad (7)$$

Therefore, the symbolic activity measurement use a numerical to symbolic interface realised by the description function  $d$ . In order to illustrate this concept, let as consider an example for potassium ( $K^+$ ) symbolic measurement. Let the measurement set be  $K^+ = [1.1 \text{ mEq/l}, 7.1 \text{ mEq/l}]$  and the symbolic set be  $S(K^+) = \{\text{small\_potassium}, \text{normal\_potassium}, \text{high\_potassium}\}$ . The translation of symbols are defined by:

$$\begin{aligned} t(\text{small\_potassium}) &= [1.1 \text{ mEq/l}, 3.1 \text{ mEq/l}] \\ t(\text{normal\_potassium}) &= [2.1 \text{ mEq/l}, 6.1 \text{ mEq/l}] \\ t(\text{high\_potassium}) &= [4.1 \text{ mEq/l}, 7.1 \text{ mEq/l}] \end{aligned}$$

and the description of measurements comes directly from the definition. For example:

$$\begin{aligned} d(1.87 \text{ mEq/l}) &= \{\text{small\_potassium}\} \\ d(4.23 \text{ mEq/l}) &= \{\text{normal\_potassium}\} \\ d(4.98 \text{ mEq/l}) &= \{\text{normal\_potassium}, \text{high\_potassium}\} \end{aligned}$$

A fuzzy-symbolic ion activity measurement concept is defined as the association of a symbol  $s$  and a fuzzy translation which associates any symbol  $s$  of  $S$  with a fuzzy subset of  $A$ . It is characterised, for all  $a \in A$ , by its membership function denoted  $\mu_{t(s)}(a)$ . The fuzzy description

associates any ion activity measurement  $a$  of  $A$ , a fuzzy subset of symbols. It is characterised, for all  $s \in S$ , by its membership function denoted  $\mu_{d(a)}(s)$ . The relation between the membership function of a fuzzy description and the corresponding fuzzy translation comes directly from the fundamental relation between the translation and description, as in Fig.6.

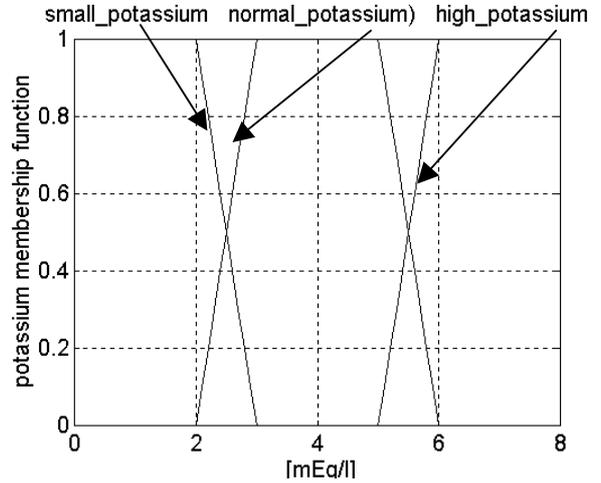


Fig.6 – Potassium fuzzy-symbolic measurement

Using an aggregation of measurements performed by fuzzy-symbolic ion activity sensors and special software, the qualification of the essential parameters (hematocyte, glucose, ionized calcium normalized at pH 7,4, hemoglobin and so one) is possible.

For example, by fuzzy-symbolic measuring of the Na activity, and of the resistance of the test solution R, it is possible to calculate the hematocyte:

$$H_{cr} \% = 1 - \frac{1}{R \frac{Na^+}{240}} 100 \quad (8)$$

### 4. THE MEASUREMENT SYSTEM

The configuration of a multi-sensor, computer piloted ion activity measuring system, capable of offering such information is described in Fig. 7.

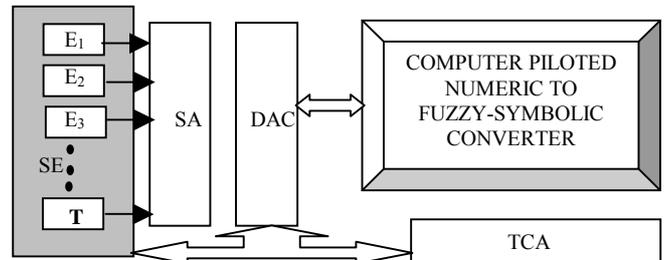


Fig.7 – The measurement system

It includes a set of electrodes SE sensitive to: sodium, potassium, chlorine, ionized calcium, hydrogen, oxygen,

carbon dioxide, impedance, a temperature sensor T of the type PT100, separation amplifier SA, a data acquisition card DAC of the type LabPC+, a Pentium PC and a time-delay sensor drive and control assembly TCA.

## 5. RESULTS

Different solutions of human blood have been measured in parallel with our system and with classical photometric method. Several results of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  are given in Table I. The normal and pathologic values of these ions are presented in Table II.

Table I – Several results for  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$

Number of sample	Age of patient	Photometric result (mEq/l)			Fuzzy-symbolic result		
		$K^+$	$Ca^{2+}$	$Mg^{2+}$	$K^+$	$Ca^{2+}$	$Mg^{2+}$
1.	19	3.91	4.3	2.17	N_P	S_C N_C	N_M
2.	29	4.22	4.7	2.30	N_P	N_C	N_M
3.	31	3.96	4.9	2.02	N_P	N_C	N_M
4.	42	3.48	4.9	1.85	S_P N_P	N_C	N_M
5.	58	4.13	4.5	1.80	N_P	S_C N_C	N_M
6.	52	3.56	4.6	1.61	S_P N_P	N_C	N_M
7.	61	3.36	4.2	1.22	S_P	S_C	S_M
8.	66	3.49	4.4	1.92	S_P N_P	S_C N_C	N_M
9.	18	4.36	4.9	1.60	N_P	N_C	N_M
10.	21	3.39	4.7	1.26	S_P	N_C	S_M N_M

Table II – Normal and pathologic value for  $Ca^{2+}$  and  $Mg^{2+}$

Tip of ions	Normal values (mEq/l)	Pathologic values (mEq/l)	
		Small	High
$K^+$	3.5 ... 5	3 ... 3.5	3.5 ... 4
$Ca^{2+}$	4.5 ... 5.5	4 ... 4.5	5.5 ... 6
$Mg^{2+}$	1.3 ... 2.9	0.8 ... 1.3	2.9 ... 3.4

In the Table I the fuzzy-symbolic values **S\_P**, **N\_P**, **H\_P**, **S\_C**, **N\_C**, **H\_C**, **S\_M**, **N\_M**, **H\_M** are respectively the abbreviations of the fuzzy-symbolic values **small\_potassium**, **normal\_potassium**, **high\_potassium**, **small\_calcium**, **normal\_calcium**, **high\_calcium**, **small\_magnesium**, **normal\_magnesium**, **high\_magnesium**.

Using our system and a classical method, other solutions have been used to study the hematocyte. In the Table IV is given several results of these investigations. The normal and pathologic values of the hematocyte are presented in Table III.

Table III – Normal and pathologic value for hematocyte

Normal values (%)		Pathologic values (%)			
		Small		High	
Men	Women	Men	Women	Men	Women
40...50	37...47	23...40	20...37	50...70	47...67

Table IV – Several results for hematocyte investigation

Number of sample	Age of patient	Patient	Classical result (%)	Fuzzy-symbolic result
1.	22	Woman	44	normal_hematocyte
2.	30	Men	41	small_hematocyte normal_hematocyte
3.	52	Men	34	small_hematocyte
4.	38	Woman	37	small_hematocyte normal_hematocyte
5.	62	Woman	33	small_hematocyte
6.	68	Woman	41	normal_hematocyte
7.	48	Men	45	normal_hematocyte
8.	77	Men	36	small_hematocyte
9.	35	Men	28	small_hematocyte
10.	62	Woman	40	normal_hematocyte

## 6. CONCLUSIONS

In this paper a fuzzy-symbolic method for ion activity measurement and the configuration of a multi-sensor computer piloted measuring system, capable of offering this result and other useful collateral information is presented. Our system can be used in the clinical laboratory where the number of analyses is high, and most of such analyses are in normal limits.

The possibility to evaluate the ion activity level in this way has the potential to contribute significantly to the increase of the rate of laboratory investigations as well as to guide the doctors toward the most effective treatment options.

Using special supplementary software, several directions of these treatment options can be given by our system.

## ACKNOWLEDGMENTS

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