ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 8, pp. 1384−1389. © Pleiades Publishing, Ltd., 2009.
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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

"Electronic Tongue" Integrated Sensor System Based on an Array of Ion-Selective Field-Effect Transistors for Multicomponent Analysis of Liquid Media

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Received April 20, 2009

Abstract—Results obtained with an "electronic tongue" device based on an array of ion-selective field transistors integrated into a flow-injection system are presented. The component concentrations in mineral waters from Spanish manufacturers are analyzed. Processing of analytical signals by the partial least squares method improves the accuracy of component determination in mineral waters of close compositions. A single chip integrates sensors sensitive to pH, K^+, Na^+, Ca^{2+}, and Cl^- ions. Mineral waters are classified and the concentrations of the main components are calculated with an error not exceeding 10%.

DOI: 10.1134/S1070427209080126

Multicomponent analysis of liquid media is a complicated task because of the insufficient selectivity of the sensors that have been developed so far. Use of high-dimension mathematical methods can solve this problem in numerous cases [1], including that with potentiometric sensors [2–4]. In this case, the analytical signal is represented as a data array in which sensor potentials under equilibrium conditions correspond to each solution. At the same time, it has been shown [5] that the curve describing the variation of the potential with time can furnish an additional information in a calculation of the component concentrations.

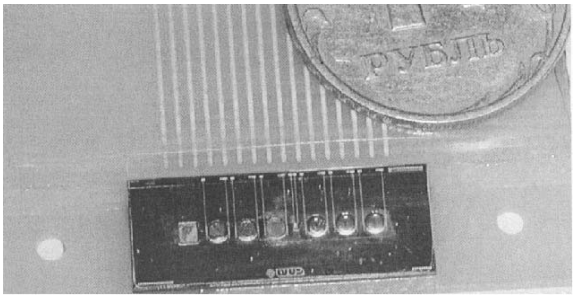

Fig. 1. Multichip with six ISFET sensors with polymeric membranes.

In this communication, it is suggested to use additional parameters, which, in the case of a flow-injection analysis (FIA), are represented by a number of potentials recorded with ion-selective field-effect transistors (ISFETs), when passing a sample through a multichip. In the given case, the variation of the potential depends on hydrodynamic conditions of an experiment and may differ from the equilibrium value because of the difference between kinetic parameters of reactions of ions with the membrane surface.

EXPERIMENTAL

In this study, a device of the "electronic tongue" type is represented by an array of ISFET sensors fabricated on a single substrate. A polymeric layer of an ion-sensitive membrane is deposited onto each sensor (except the pH-ISFET) [6]. Figure 1 shows the outward appearance of an array of sensors. The dimensions of the silicon substrate are 20.71 × 8.00 mm. The sensors have a three-layer structure: bottom layer (silicon wafer) onto which a silicon oxide layer is deposited, and an upper layer (thin semiconducting silicon film). The technology developed allows electrical insulation of each of the ISFET sensors

and thereby enables independent measurement of their potentials. In this study, five out of the available six ISFET sensors were used.

The last of the sensors deposited onto the substrate is the electrode for measuring the solution conductivity, in the form of thin alternating platinum strips. The deposition technology of the platinum electrode employs an electron beam, which, in turn, affects the standard electrode potential of ISFET sensors. To diminish this effect, the technological cycle includes an annealing stage intended to restore the electrode potential [7].

The electrical contacts are protected with a photopolymerizable material to preclude short-circuiting on submerging the substrate with the multichip in a solution. The final stage is deposition of ion-sensitive membranes sensitive to K^+, Na^+, Ca^{2+}, and Cl^- ions. The process of fabrication of photopolymerizable membranes with the corresponding ionophores has been described previously [8–11].

The array of ISFET sensors was integrated with a flow-injection system developed on the basis of components manufactured by FIALab company (USA). The flow-through cell with a volume of 10 μl was hermetically attached to the multichip. It included an ORION reference electrode (RE) mounted at the cell outlet. This precluded the possible influence of the concentrated solution of the RE on the potential of the sensors and, in particular, on the chloride-sensitive ISFET. The sensor potentials were recorded with an ISFET-meter developed at the Institute of Microelectronics (Spain). The response of the sensors was recorded, valves and pumps were controlled, and measurement results were processed using a software written in Visual Basic.

In the study, two types of measurements were made, with mathematical models developed for identification of water samples and for quantitative analysis of mineral water components.

The main goal in the quantitative analysis of mineral water was to determine whether waters with close contents of sodium, potassium, and chloride ions can be identified without preliminary sample preparation. For this purpose, a multicomponent calibration was carried out against a set of solutions in which the content of each of the components was varied within a certain range.

Between measurements, the chip was stored in a mixture of NaCl + KCl solutions with a concentration of 10^{-3} M. Prior to measurements, the chip was washed with distilled water. The measurement results were processed by the partial least-squares (PLS) method implemented using such software packages as Unscrambler 7.8 (CAMO, AS) and TANAKA. The process of the multicomponent calibration was described in detail [12, 13].

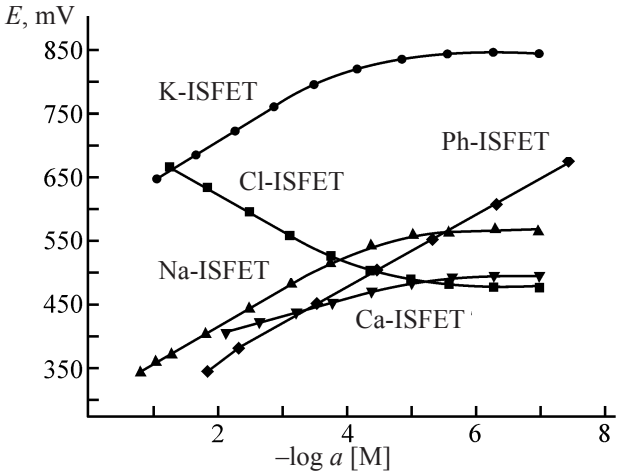

Fig. 2. Calibration dependences for ISFET sensors in individual solutions. (*E*) Solution potential and (a) activity of ions in solution.

Prior to measurements with real samples, the potentials of each of the sensors were measured in individual solutions in the concentration range 10^{-7}–10^{-1} M. The average slope ratio, measured during 15 days, for K^+, Na^+, and Cl^- ISFETs was 54–56 mV dec^{-1}; 55.2 mV per pH unit in the pH range 2–8 for the pH-ISFET; and 28 mV/pCa for the Ca^{2+} ISFET. The results of calibrations for each of the ions are shown in Fig. 2.

The response time of each of the sensors was determined by recording ISFET potentials at a continuous flow of individual solutions of the ions. At a flow rate of 250 μl min^{-1} and on replacing the solution with a more concentrated solution (10^{-4}–10^{-3} M), the potential was stabilized in 1 min and constituted no less than 95% of the equilibrium value.

Determination of the optimal parameters of a flow-injection analysis. A set of experiments aimed to determine the optimal FIA parameters was performed, with the flow rate and sample volume varied. The analytical characteristics of the sensors in flow-through and stationary conditions are different because, in the first case, measurements are made under nonequilibrium conditions and a "kinetic" factor is important. Consequently, the signal depends on parameters of the flow-through system. As a rule, the flow rate and the

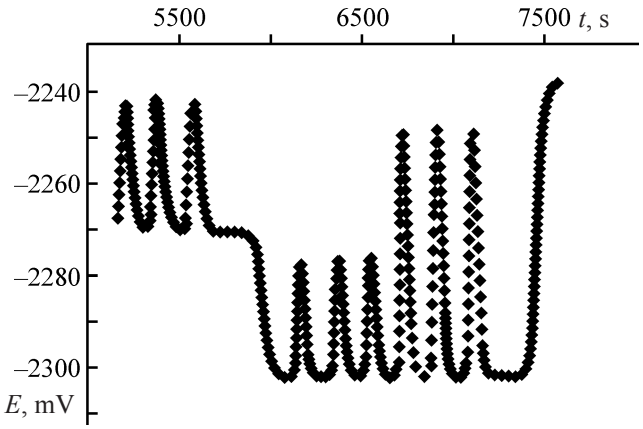

Fig. 3. Response of K-ISFET at a flow rate of 250 μl min^{-1} and sample volume of 100 μl. (*E*) Solution potential and (*t*) response time; the same for Fig. 4.

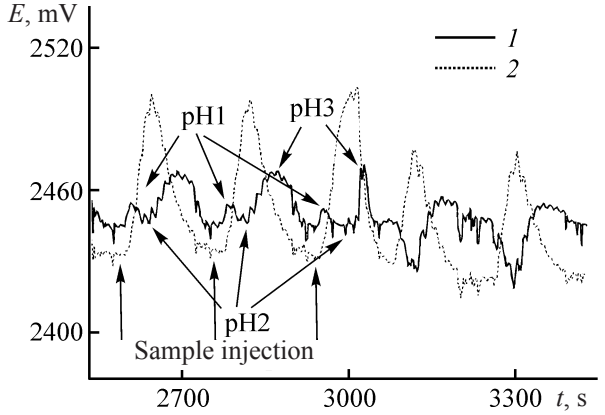

Fig. 4. Peak shapes for (*1*) pH-ISFET and (*2*) sensor for chlorine.

sample volume are optimized to provide a sufficient time of contact between a sample and the membrane surface in order to obtain the maximum possible signal. At the same time, a shorter contact duration occasionally makes it possible to improve the detector selectivity via "kinetic discrimination." In the case in question, it was necessary to provide to each sensor of the array a sufficient contact time for a response to the components present in solution to be obtained.

In the experiments, the sample volume was varied from 100 to 500 μl. At sample volumes smaller than 100 μl, the signal became irreproducible and its amplitude was 60–70% of the equilibrium potential. This may be due to partial and uncontrollable dilution of a sample in its transport through pipes. At volumes exceeding 500 μl, the peak width and, accordingly, the analysis duration substantially increased (to more than 7 min for a single sample).

Figure 3 shows examples of peaks for a K-ISFET at a flow rate of 250 μl min^{-1} and a sample volume of 100 μl. The maximum height of the peak is 80% of the equilibrium potential, but, if the concentrations of potassium ions in two solutions differ by more than an order of magnitude, the value reaches 95% of the equilibrium potential. Hence follows a conclusion that, to improve the reproducibility of the results and obtain potentials close to those under stationary conditions, it is necessary that the content of components in calibrating solutions should be close to that in real samples.

Thus, the following optimal FIA parameters were chosen: flow rate 100 μl min^{-1} and sample volume 100 μl. These parameters may vary with the design of a flow-through cell, pipe diameters, and component concentrations, but their ratio, as a rule, remains constant.

Quantitative analysis of mineral water. The reproducibility of ISFET signals in a multichip in solutions with the same component concentrations was 1 mV. During a day, the drift for the sensors did not exceed 2–3 mV. Several samples of mineral waters produced by Spanish manufacturers, with about the same contents of sodium, potassium, calcium, and chloride ions, were chosen for a qualitative analysis. Of seven mineral water brands, only two had somewhat higher pH values (Lanjaron) and higher sodium and potassium concentrations (Fuente Liviana). Between measurements, a $NaHCO_3$ solution (1 M + 1 M KCl) was passed through the flow-through cell. The concentrations in this solution were higher than those in mineral waters, and, therefore, the sensor signals had negative values.

Figure 4 shows an example of the pH-ISFET response. It can be seen from the plot that, as a sample is passed through the detector, the peak has three extrema. After the sample is injected, the signal increases during 5–10 s, then falls (8–15 s), and then again increases (15–20 s). For comparison, the same plot shows the response of achloride-sensitive ISFET with a peak shape typical of FIA. Reasons for the uneven response for the pH-ISFET are not quite clear, but reproducible and possibly due to the reaction of the pH-ISFET to presence of certain impurities in real sample. To construct a mathematical model by the PLS method, the following seven parameters were used as input data: heights of K^+, Na^+, Ca^{2+}, and Cl^- ISFET peaks and three heights of pH-ISFET peaks.

Figure 5 shows the distribution over the main

Determination of sodium, potassium, calcium, and chlorine ions and pH value with an array of ISFET sensors ("electronic tongue")

Mineral water	Na^+		K^+		PH		Ca^{2+}		Cl^-	
	introduced log *c*	found	introduced log *c*	found	introduced log *c*	found	introduced log *c*	found	introduced log *c*	found
Sol de Cabras	–3.66	–3.77 (0.09) [a] –3.84 (0.15) [b]	–4.64	–4.70 (0.05) –4.76 (0.08)	7.40	7.43 (0.07) 7.38 (0.07)	–2.83	–2.79 (0.05) –2.73 (0.08)	–3.64	–3.94 (0.18) –3.95 (0.21)
Lanjaron	–3.58	–3.58 (0.10) –3.58 (0.15)	–4.59	–4.61 (0.06) –4.60 (0.08)	6.77	6.75 (0.07) 6.78 (0.07)	–3.14	–3.09 (0.06) –3.11 (0.09)	–4.25	–4.33 (0.20) –4.35 (0.22)
Font Vella	–3.24	–3.31 (0.10) –3.32 (0.15)	–4.48	–4.48 (0.05) –4.49 (0.08)	7.62	7.56 (0.07) 7.59 (0.07)	–2.99	–2.97 (0.06) –2.96 (0.09)	–3.51	–3.64 (0.19) –3.68 (0.21)
Evian	–3.62	–3.50 (0.10) –3.47 (0.14)	–4.72	–4.68 (0.05) –4.65 (0.08)	7.20	7.19 (0.07) 7.19 (0.06)	–2.71	–2.77 (0.06) –2.83 (0.08)	–4.21	–3.94 (0.19) –3.94 (0.21)
Viladrau	–3.38	–3.39 (0.10) –3.51 (0.15)	–4.45	–4.41 (0.05) –4.40 (0.08)	7.40	7.49 (0.07) 7.56 (0.07)	–3.21	–3.16 (0.06) –3.14 (0.08)	–3.86	–3.84 (0.19) –3.79 (0.21)
Font Dor	–3.56 –4.46	–3.53 (0.10) –3.53 (0.15)	–4.34	–4.36 (0.05) –4.36 (0.08)	7.70	7.67 (0.07) 7.59 (0.07)	–3.23	–3.26 (0.06) –3.28 (0.08)	–3.89	–3.79 (0.19) –3.89 (0.21)
Fuenta Liviana		–4.41 (0.10) –4.27 (0.15)	–4.89	–4.85 (0.06) –4.77 (0.08)	7.42	7.43 (0.07) 7.45 (0.07)	–2.79	–2.81 (0.06) –2.89 (0.09)	–4.30	–4.23 (0.21) –4.13 (0.22)

[a] Results of measurements performed using seven parameters.
[b] Results of measurements performed using five parameters.

components for seven mineral water brands. The principal direction for the first component (PC1) corresponds to variation of the pH of the medium, because just the difference in pH from other mineral waters is characteristic of the Lanjaron brand. The second main component mostly corresponds to variation of the sodium concentration with a water brand (the concentration grows from Fuenta Livana to Font Vella).

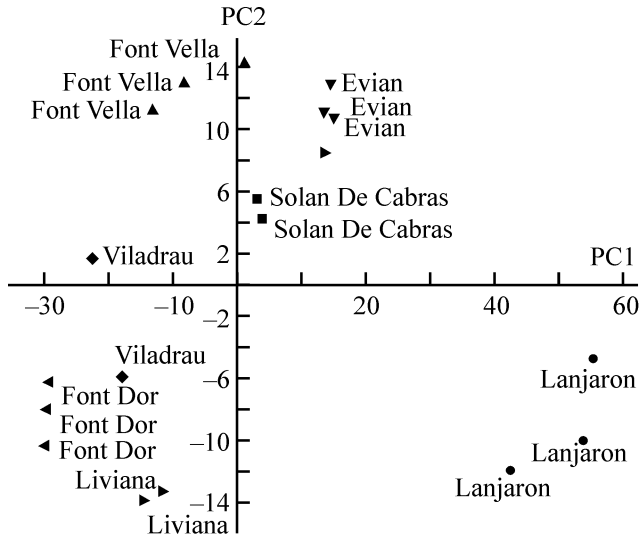

Fig. 5. Zone distribution for mineral waters, calculated using the PLS method.

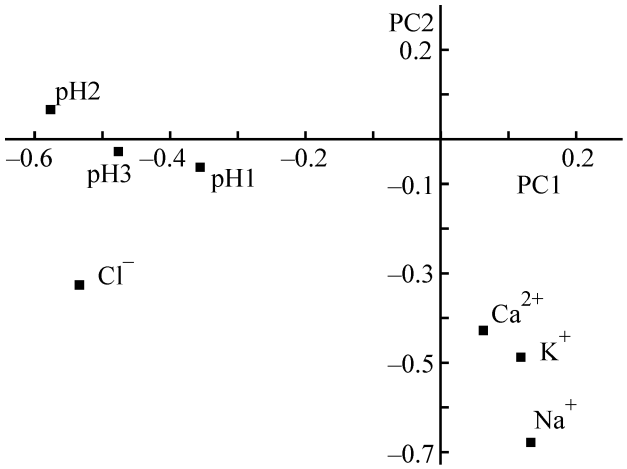

Fig. 6. Weight distribution for each of the sensors in the PLS model.

The same conclusion can be made from Fig. 6, which shows a relative contribution of each of the sensors to the mathematical PLS model. Comparison of the three pH parameters (pH1, pH2, pH3) shows that pH2 makes the greatest contribution because it is the main peak obtained when measuring a sample.

Quantitative analysis of mineral waters. The concentrations of the components of interest were calculated using to PLS models. The first used only five parameters as input data (number of individual ISFET sensors), and the second, seven parameters, including two additional parameters from the pH-ISFET. The results of measurements using two models are listed in the table. It can be seen that making larger the number of parameters at the same number of measurements gives a higher accuracy of determinations. For example, the measurement error was 5–7% for K^+, Ca^{2+}, and pH-ISFET, 10% for Na+ ions, and 19% for Cl– ions.

Making greater the number of parameters is possible not only for pH-ISFET, but also for other sensors. For example, if the potential is recorded every 1 s when passing a sample through the detector for 1 min, 60 potentials will correspond to each sample, which gives, for 5 ISFETs, a total of 300 parameters for a single sample. These potentials will be for the most part correlated, but the PLS method can be used to distinguish independent components and calculate the regression formula for finding unknown concentrations.

CONCLUSIONS

(1) A multichip with integrated sensors based on ion-selective field-effect transistors can be used both for a qualitative analysis of mineral waters with close compositions and for qualitative determination of sodium, potassium, calcium, and chloride ions and hydrogen.

(2) Use of a flow-injection analysis makes it possible, on the one hand, to automate the process and, on the other hand, to perform experiments in the dynamic mode in which the sensor potential depends not only on the concentration of certain ions in a sample, but also on the difference of responses in the equilibrium and nonequilibrium modes.

(3) The introduction of new “dynamic” parameters extends the capacity of analysis and improves the accuracy with which components of interest are determined.

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