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NONSPECIFIC SENSOR ARRAYS ("ELECTRONIC TONGUE") FOR CHEMICAL ANALYSIS OF LIQUIDS

(IUPAC Technical Report)

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Abstract: The history of the development of potentiometric sensors over the past century demonstrates progress in constructing single, discrete (i.e., separate, to distinguish from sensor arrays) ion sensors, which have been made as selective as possible. Only a few types reveal high selectivity. However, easy measurement procedure, with low cost and availability, give rise to the search for new ways for their successful application. The present document describes a new concept for application of potentiometric multisensor systems, viz., sensor arrays for solution analysis, and the performance of this new analytical tool—the "electronic tongue". The electronic tongue is a multisensor system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on the pattern recognition (PARC) and/or multivariate analysis [artificial neural networks (ANNs), principal component analysis (PCA), etc.]. Definitions of the multisensor systems and their parameters are suggested. Results from the application of the electronic tongue, both for quantitative and qualitative analysis of different mineral water and wine samples, are presented and discussed.

Keywords: Sensors; chemical sensors; electronic tongue; potentiometric sensors; technical report; IUPAC Analytical Chemistry Division.

1. INTRODUCTION

Selectivity of potentiometric sensors, such as ion-selective electrodes (ISEs), is defined by the selectivity coefficient, $K_{i,j}$, for the primary ion, i, against the interfering ion, j, in the Nikolsky–Eisenman equation

$$E = E^{\circ} + \frac{RT}{z_i F} \ln \left[a_i + \sum_j K_{ij}(a_j)^{z_i/z_j} \right] \qquad (1)$$

where a_i and a_j are activity of the primary and interfering ion, respectively; $K_{i,j}$ is the selectivity coefficient; E° is the sum of the standard potential of the electrode and the junction potential; E is the potential difference for the electrochemical cell composed of the ion-selective and reference electrode; z_i and z_j are charge numbers of the primary and interfering ion, respectively; and R, T, and F have their usual meanings. This equation predicts a linear dependence of the sensor response, E, on the logarithm of a function of the activity of the ions in solution.

Selectivity is very important and is high for some types of sensors. But in complex solutions (i.e., those containing many ions to which the electrodes are responsive), the measured potential difference may not obey the Nikolsky–Eisenman equation. Application of low-selective sensor arrays along with modern mathematical procedures for signal processing, which involve pattern recognition (PARC) and multivariate analysis, provides a solution for the selectivity problem.

The history of potentiometric sensors can be divided into four periods [1,2] (Table 1). In the first three of these periods, selective sensors were developed. In the most recent period, new analytical tools called the "electronic nose" and "electronic tongue" were developed.

Table 1 Milestones in potentiometric sensor development.

I. 1906–1937. pH glass electrode and ion-exchange theory	Refs.
1906 Cremer: dependence of the cell potential difference on pH (glass membrane)	[39]
1909 Haber, Klemensiewicz: development of a glass electrode	[40]
1936 Beckman: commercialization of pH-meter	[41]
1937 Nikolsky–Nikolsky equation and theory of operation of a glass electrode	[42,43]
1937 Kolthoff: crystalline "electrode"	[44]
1937 Nikolsky: crystalline membrane	[45]

II. 1961–1969. Conventional ISEs and biosensors	
1957 Eisenman: properties of glass electrode and Eisenmann–Nikolsky equation	[46]
1958 Severinghaus, Bradley: gas-sensitive electrodes	[47]
1961 Pungor: heterogeneous solid ISE	[48]
1961 Eisenman: theory of glass electrode	[49,50]
1962 Seiyama, Taguchi: semiconductor gas sensor	[51–53]
1966 Frant, Ross: LaF_3–electrode	[54]
1966 Simon: liquid ISE with neutral carrier	[55]
1967 Ross: ion-exchange membrane	[56]
1969 Guibault, Montalvo: potentiometric biosensor	[57]
1969 Baker, Trachtenberg: chalcogenide glass membrane for ISE	[58]
1971 Moody, Thomas: PVC-based ISEs	[59]

III. 1970 to present. Microelectronics in sensor development	
1970 Bergveld: ISFET	[60]
1975 Lundstrom: gasFET	[61]
1976 Schenck: immunoFET	[62]

IV. 1982 to present. Multisensor arrays and sensor systems	
1982 Persaud, Dodd: electronic nose	[4]
1992 Toko: "taste" sensor	[63]
1995 Vlasov, Legin, D'Amico, Di Natale: electronic tongue	[5]

The aim of the present report is to show more general approaches to the analytical characteristics of the sensor array of an electronic tongue and to recommend relevant definitions.

2. GENERAL CONCEPTS

The general concepts of the electronic tongue and electronic nose used for analysis of liquids and gases, respectively, are similar. They involve application of an array of nonspecific or low-selective sensors in order to produce analytically useful signals during the analysis of multicomponent matrices. The rationale for application of low-selective sensors is based on an analogy to biological organization of the olfactory and taste systems in mammals. In the regions of the nose and tongue, there are millions of nonspecific receptors that respond to different substances present in the gas and liquid phases. However, only about 100 different types of olfactory receptors are known, while several dozens were identified in the taste buds on tongues of mammals. The taste and odor signals from the receptors are transmitted to the brain where they are processed by nets of neurons. As a result, the image of the sensed object is created.

The idea of reproducing artificially the natural response of a human to environmental stimuli was published in 1943 [3]. It can be treated as one of the first steps to build an "electronic brain" and artificial intelligence based on neural computing. The first analytical device that resulted from these trends

was an electronic nose (1982) [4] applied to gas analysis. The next was an electronic tongue, which was introduced in 1995 [5] and which can be considered as a promising device in quantitative and qualitative analysis of multispecies solutions. Principal features of the two new sensor devices, i.e., the artificial nose and tongue, are: (i) application of sensor arrays comprising a certain number of nonspecific, low-selective chemical sensors, (ii) application of PARC, including artificial neural network (ANN), principal component analysis (PCA), etc., for processing of high-dimension signals produced by the sensor arrays. However, the compositions and properties of the sensing materials used for electronic nose and electronic tongue sensor arrays differ significantly. Therefore, development and consideration of multisensor systems for analysis of gaseous and liquid matrices should be performed separately rather than simultaneously.

3. CLASSIFICATION AND DEFINITIONS OF CHEMICAL SENSOR ARRAY DEVICES

In the literature, the following definition of the electronic tongue can be found [2]:

The electronic tongue is an analytical instrument comprising an array of nonspecific, low-selective, chemical sensors with high stability and cross-sensitivity to different species in solution, and an appropriate method of PARC and/or multivariate calibration for data processing. Stability of sensor behavior and enhanced cross-sensitivity, which is understood as a reproducible response of a sensor to as many species as possible, are of primary importance. If properly configured and trained (calibrated), the electronic tongue is capable of recognizing the qualitative and quantitative composition of multispecies solutions of different natures [2].

One can consider the electronic tongue a device for qualitative and quantitative analysis of complex solutions. The history of application of various sensor arrays for solution analysis is described in [2].

The history of development and features of the electronic nose are described in [6].

4. SENSING MATERIALS FOR SENSOR ARRAYS

Different types of chemical sensors can be used in the sensor arrays operating in the electronic nose and electronic tongue.

In the electronic nose, usually some metal-oxide semiconductor materials (e.g., doped SnO_2) [7–9], conducting polymers (e.g., polypyrrole) [10–12], or metalloporphyrin films [13–14] are used.

Sensors based on various sensing principles can be employed in electronic tongues, the most widespread being potentiometric, amperometric, or optical sensors [15]. Sensing materials used in electronic tongues may also vary significantly. Chalcogenide and oxide glasses and crystalline materials have been used as membranes of potentiometric sensors [2,16], and noble metals [17] have been used mostly for amperometric signal detection. Sensing materials based on plasticized organic polymers containing different active substances have been employed for both potentiometric [2,15,18] and optical sensors [19].

5. ANALYTICAL CHARACTERISTICS OF THE ELECTRONIC TONGUE

The main criteria for application of a sensor in a sensor array are its low selectivity and high cross-sensitivity instead of high selectivity. Cross-sensitivity is understood here as the ability of a sensing element to respond reproducibly to a number of different analytes in solution and/or to produce a stable integrated response in the multispecies systems being analyzed. A dedicated special empirical method and experimental procedure for estimation of the sensor cross-sensitivity has been proposed [20]. Three parameters were suggested for characterization of sensor cross-sensitivity: average slope of sensor response reproducibility and nonselectivity factors (for details, see [20]). Besides cross-sensitivity, such terms as "low-selective" or "nonspecific" are used to describe sensor properties. These terms mean that

sensors are not exclusively selective for one particular species in solution, but may respond to different analytes. Use of these terms is consistent with recently published IUPAC recommendations on selectivity [21].

Another important feature of sensors to be included in a multisensor system is the difference of their responses in multicomponent media. Evidently, an array of cross-sensitive sensors producing identical signals in the analyzed media would be of little value. Thus, besides being cross-sensitive, the sensors of the array should be different, i.e., they should display different responses to the same set of substances. Resulting sensor arrays should produce a "spectrum-like" response in multicomponent media, allowing recognition or quantitative analysis of these media. Responses of 16 cross-sensitive sensors in three different wines of B-type are shown in Fig. 1 as an example. There is no theoretical background so far for an algorithm of choosing different (and most promising) sensors for the electronic tongue, and this process still remains an empirical procedure.
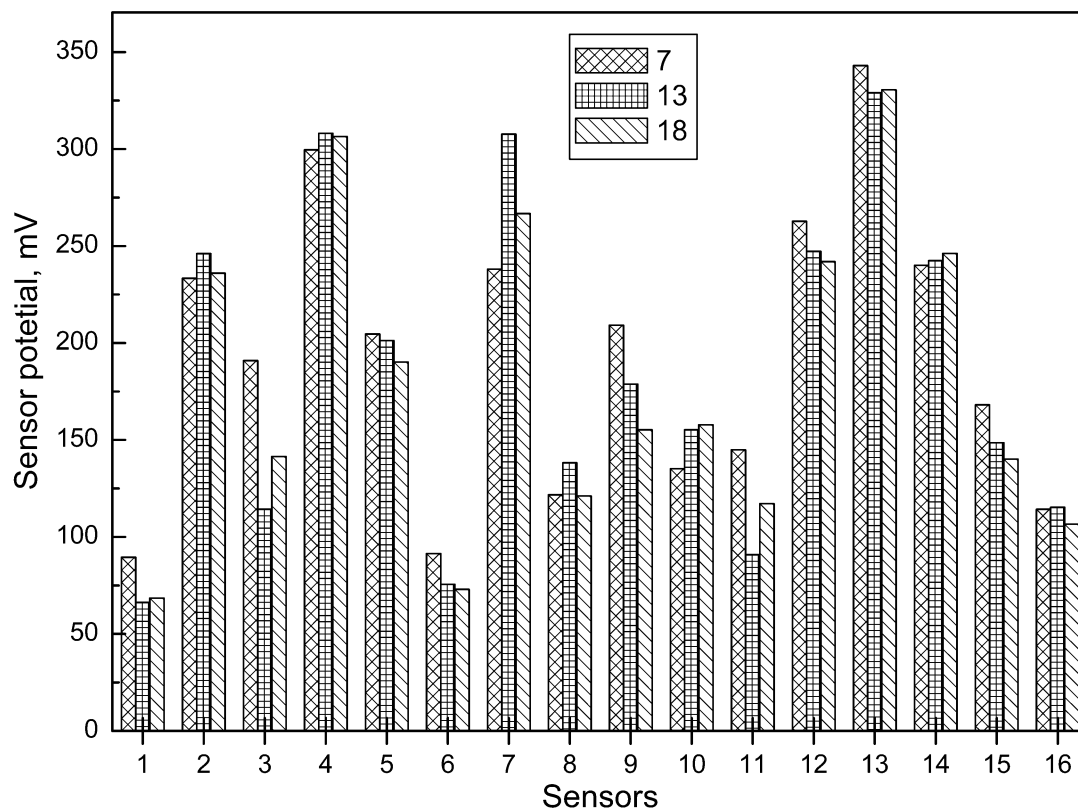
Fig. 1 Responses (potential values in mV) of the sensors of the electronic tongue in wine samples of denomination B from three different vineyards.

A sensor array of an electronic tongue might be characterized by the same parameters as discrete sensors or ISEs including selectivity, detection limits, etc. However, these parameters may have different meanings for the sensor array and for the discrete ISEs. The parameters are more easily applicable to quantitative analysis. A method for determination of selectivity and detection limits of the sensor array was proposed in [22]. The principal differences between analytical characteristics of a discrete sensor and a sensor array are: (i) the selectivity and detection limits of a sensor array depend not only on the properties of the sensing materials used, but also on the composition of the sensor array; thus, different versions of the electronic tongue can display different analytical characteristics in the same

complex solutions under test; (ii) the selectivity and detection limits of a sensor array can be determined only after data processing is completed by using multivariate analysis, and values of the parameters may depend on the calculation method adopted [22].

In qualitative analysis, such as recognition or identification, the distinguishing abilities of an electronic tongue can be useful. This ability, and hence reliability of classification, depends also on the composition of the sensor array and the mathematical procedure adopted. Therefore, it is possible to identify the distinguishing ability of the electronic tongue and compare performance of different electronic tongue systems in the same set of solutions using the same measurement protocol, as demonstrated in [23].

6. ANALYTICAL PROCEDURE

The number of sensors used in the sensor arrays depends on the analytical task and on how many different sensing materials are available. The number of sensors in the array may vary from 4 to 40 [15]. Typically, the sensor array contains an excessive number of unit sensors, and thus is applicable for different analytical tasks. If this is the case, different smaller sub-arrays of sensors can be considered during data processing. This approach permits one to reduce the size of data sets for processing without a significant loss of analytical information. In some cases, sensors based on different principles of signal transduction (e.g., potentiometric and amperometric) may be used simultaneously in the same sensor array [24]. An example of measuring procedure for the electronic tongue based on potentiometric sensors is described below. Potentiometric sensors were chosen for the example because to date they are the most widespread type of sensors used in electronic tongue systems.

Sensors made of chalcogenide glass and PVC-based polymer membranes with enhanced cross-sensitivity can be incorporated into a sensor array as described in [15,16,25–29 and refs. cited therein]. A number of conventional ISEs, e.g., pH glass electrode, sodium- and chloride-selective electrodes, may also be included in the system [16].

Potentiometric measurements should be carried out using a multichannel voltmeter with high input impedance. Values of the sensor potential should be measured against a conventional Ag/AgCl reference electrode and stored as computer data files. Sample pretreatment prior to measurements is not necessary.

The following procedure for potentiometric measurements with a sensor array can be recommended. In [25–27], measurements performed on six Italian mineral waters, A–F, and tap water from the Rome water supply system are described. The measurements were performed in seven experimental sessions, one session per day, over two weeks. In each session, each sample was measured at least three times, each time with a new portion. Two water samples were carbonated (E and F), therefore excess CO_2 was removed by intensive stirring prior to measurements. After a day of measurements, no changes were observed which could be attributed to carbonation, viz., the pH change was less than 0.05. A new bottle (sample) was used on each day of measurement. The final data set consisted of 63 calibration points, also used for random full cross-validation, while 84 samples were considered as tests.

In the next stage of experiments, pieces of strawberry (4 to 5 g of fruit per 1 dm^3 of water) were introduced into the bottles of two different mineral waters (i.e., C and D) in order to induce some disturbance in the system. On the fourth day, measurements were performed on both the contaminated and noncontaminated water samples.

In another experimental session, measurements were performed on different types of dry wines [26–27]. First, the optimum measurement time was determined for red and white wine from the same region. Then, 20 red wine samples of the same brand but from different vineyards were analyzed. For a given wine sample, all individual sensors of the array reached a stable potential (within 0.1 mV/min) in 15 min. Reproducibility of the sensor potential during two weeks of experiments was about 3 to

4 mV. No noticeable drift of sensor potential was observed. The data set saved for processing consisted of 66 points for calibration and validation as well as 60 points for test data.

7. PROCESSING OF A SENSOR ARRAY RESPONSE

In order to obtain final analytical results from the electronic tongue measurements, it is necessary to apply certain mathematical signal processing procedures. PARC methods and multivariate calibration techniques are used to analyze the response of the sensor array because output of the sensor array in a multispecies solution is complex in most cases and cannot be described by using theoretical equations (e.g., the Nernst or Nikolski–Eisenman equations). The processing of the data from the sensor array is usually performed in two ways in order to extract qualitative and quantitative information. The most frequently used methods are partial least-squares regression (PLS), PCA, and ANNs such as back-propagation, self-organizing map (SOM), etc. All these methods are described in the literature [30–35] and are recommended for processing of multivariate experimental data. The general recommendation is to use nonlinear techniques when there is nonlinearity in the data (i.e., the relationship between dependent and independent variables is nonlinear). Linear or projection methods should be used otherwise. Sensor array data rarely have a high degree of nonlinearity. Therefore, they can be fitted successfully by using projection methods, such as PCA and PLS [26]. PCA is applied for data structure exploration and visualization. Soft independent modeling of class analogy (SIMCA), which is based on modeling using PCA, is a powerful classification tool [31,33]. Most often, classification problems can be solved using SIMCA, but in certain cases, back-propagation neural net should be used. A Kohonen net can be particularly helpful in some cases for visualization purposes since it produces a 2D representation of data of any dimension [34]. Quantitative calibration can be performed using PLS or, if data are highly nonlinear, back-propagation neural net. Typically, projection methods and neural networks display similar performance [26]. However, neural networks still lack such important features as interpretation, validation, and model diagnostic tools. Therefore, projection methods are preferable. For precise performance, the data processing method should be chosen in each case [32,33]. This method selection depends upon the data structure. The data processing methods used for different tasks are discussed below.

8. ANALYTICAL RESULTS

8.1 Qualitative analysis: Recognition, classification, identification

The objectives of qualitative analysis of multispecies solutions consist of discrimination, classification, or identification of different samples. The most typical objects for this type of analysis are foodstuffs. The electronic tongue has been applied to distinguish among different types of coffee, beer, wine, mineral water, sodas, etc. [15 and refs. therein]. Application of the electronic tongue enables one to discriminate different groups of beverages (Fig. 2) [29] as well as the quality or type of each product (Figs. 3–5) [25,26,29]. Discrimination among six different samples of coffee by the electronic tongue is shown in Fig. 3 [25], the data being processed by SOM.
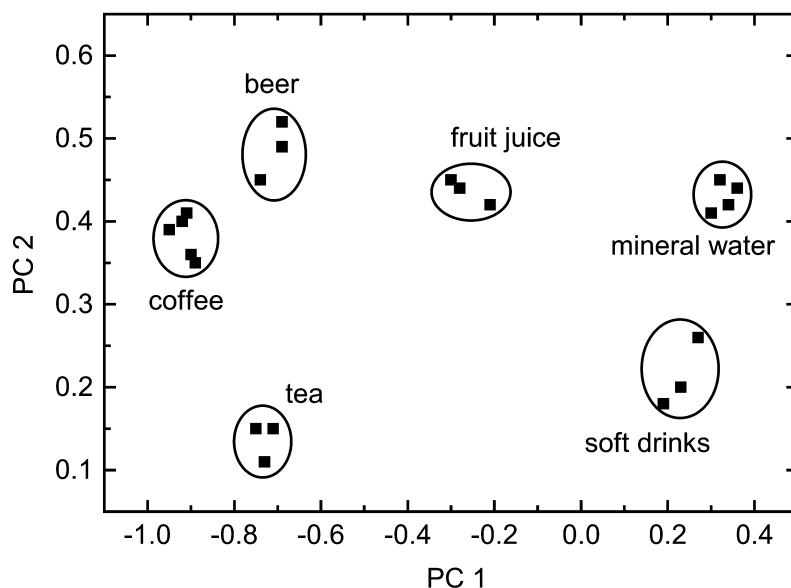
**Fig. 2** Discriminating abilities of the electronic tongue with respect to different types of nonalcoholic beverages. Data processing performed using principal species analysis (PCA). PC1 and PC2 are produced by PCA when data dimension is reduced from 30D (number of sensors in the array) to the 2D presentation shown in this picture. PC1 and PC2 are the most significant species containing the largest part of information about the analyzed beverages.
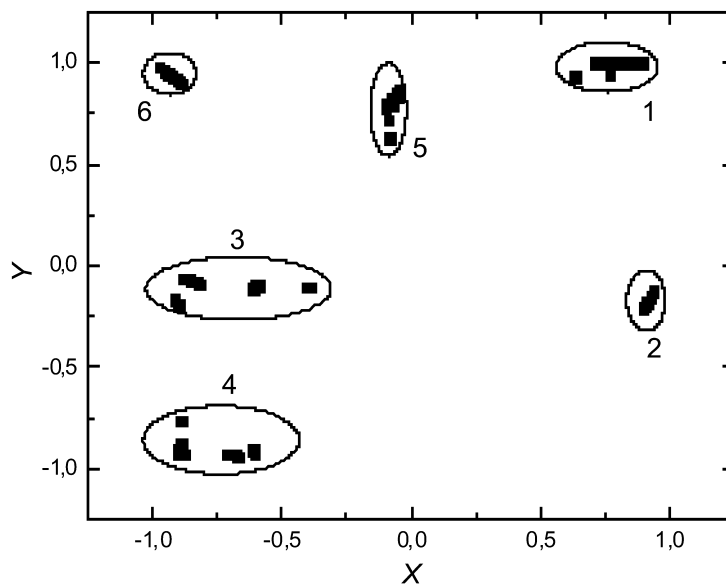
Fig. 3 Discriminating abilities of the electronic tongue with respect to similar types of beverages (6 brands of coffee). Data processing performed by using ANN–SOM. *X* and *Y* are relative coordinates produced during processing of data from the chemical sensor array.

Discrimination among different kinds of mineral waters using the electronic tongue, as described in Section 6, is shown as a PCA plot in Fig. 4 [25]. After a two-week-long measurement session, no significant drift of the sensor readings was observed. Some changes of the sensor potential values were
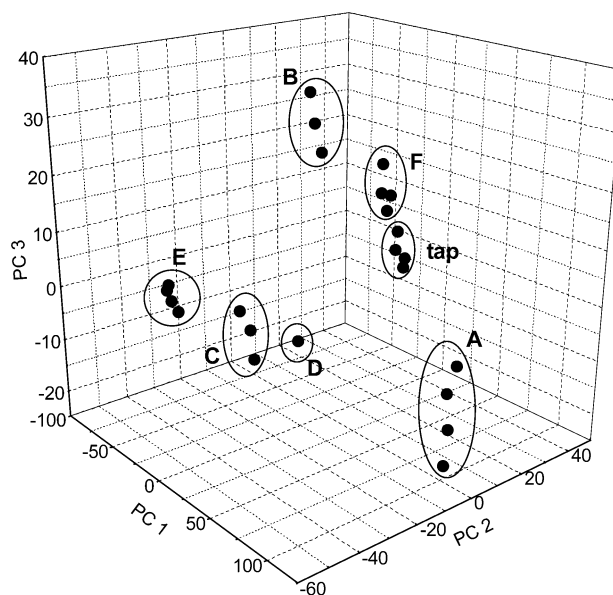
Fig. 4 Discrimination of mineral water samples and tap water by the electronic tongue. Data were processed by PCA.
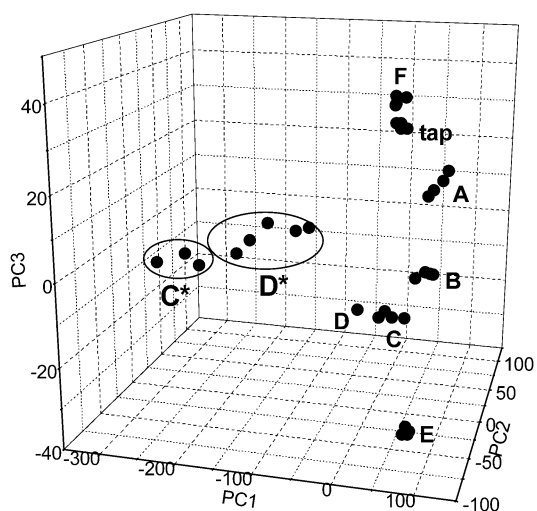
Fig. 5 Discrimination between pure mineral waters, and those contaminated by the organic matter, by the electronic tongue. Contaminated samples are marked as C* and D* on the plot.

found in the samples of water A because of the very low content of mineral species in this water. Nevertheless, each water sample could be distinguished from all others.

The electronic tongue is capable of discriminating between pure mineral water samples and those contaminated by organic matter [25]. A corresponding PCA plot, containing all water samples, is shown in Fig. 5. The contaminated mineral water samples were very different (appearing with extreme coordinates on the PCA score plot) from the pure waters of the same type as well as from all other samples. The samples of mineral water to be contaminated were chosen randomly. Thus, it is possible to conclude that contaminated water can be distinguished easily from pure using the electronic tongue. This

is true at least for the variety of the waters studied, but taking into account that the chosen water samples represent a wide range of possible compositions, the results might be generalized.

The distinguishing ability of the electronic tongue has been investigated and visualized using methods involving unsupervised learning, such as PCA, cluster analysis, and SOM. PCA is well known and widely used for processing of multidimensional data sets obtained in chemical applications [30–35]. The results of PCA are relatively easy to understand and interpret. SOM seems to be a less commonly used, but promising, method for chemical data fitting [34]. A possible advantage of SOM is related to its nonlinearity, which permits reduction of data of higher dimensions to the 2D form, while in linear PCA the number of significant species can be higher than three. These two latter methods have been compared by carrying out measurements with the electronic tongue on samples of Italian red wines [26]. Two types of wines of different denomination produced in different regions of Italy from different grapes were analyzed. These two wine types are marked as B and C. A PCA score plot discriminating between red and white wine of a C-type and 20 samples of red wine of B-type is shown in Fig. 6 [26]. The two samples of the C-type wine were easily distinguished from the B-type wine. Only samples of B-type wine are shown in the PCA score plot in Fig. 7 [26]. All 20 samples of the wine of the same brand, which are very close in taste and chemical composition, were recognized successfully by using the electronic tongue. Figure 8 shows the same results as those presented in Fig. 7, but data are processed using SOM. Obviously, the topology and relative positions of the sample images in Figs. 7 and 8 are significantly different. However, these differences are irrelevant for the analytical purpose, namely, classification, because all the samples are correctly classified and reliably distinguished by using both methods. The PCA plot (Fig. 7) seems to be more convenient for visualization, because the
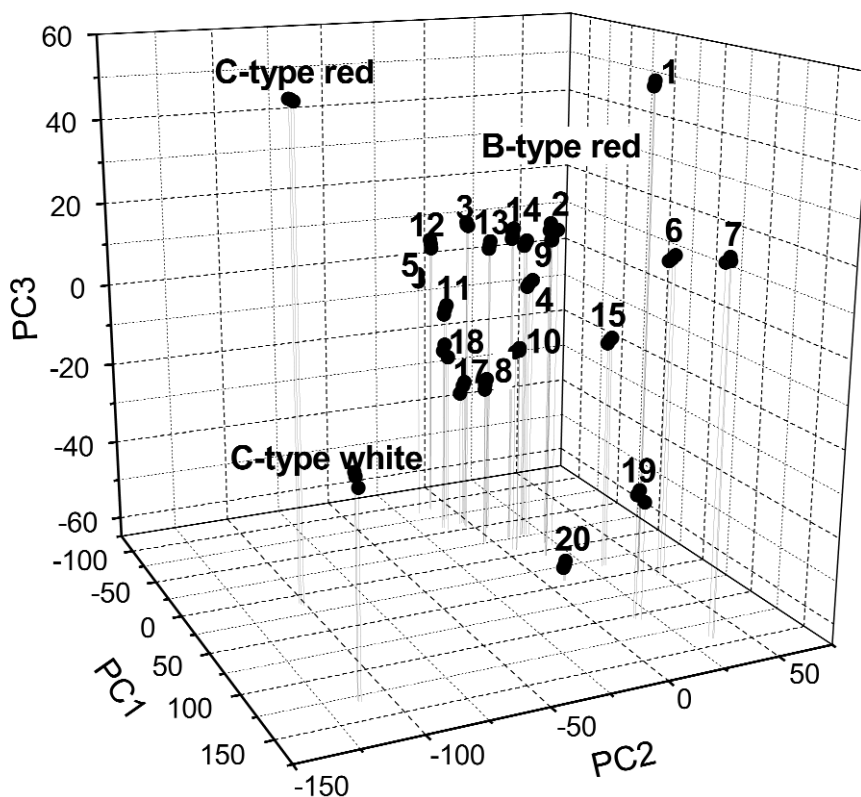
Fig. 6 A PCA score plot discriminating red and white wine of C-type and 20 samples of red wine of B-type. Two samples of C-type wines can be easily distinguished from the B-type wine.
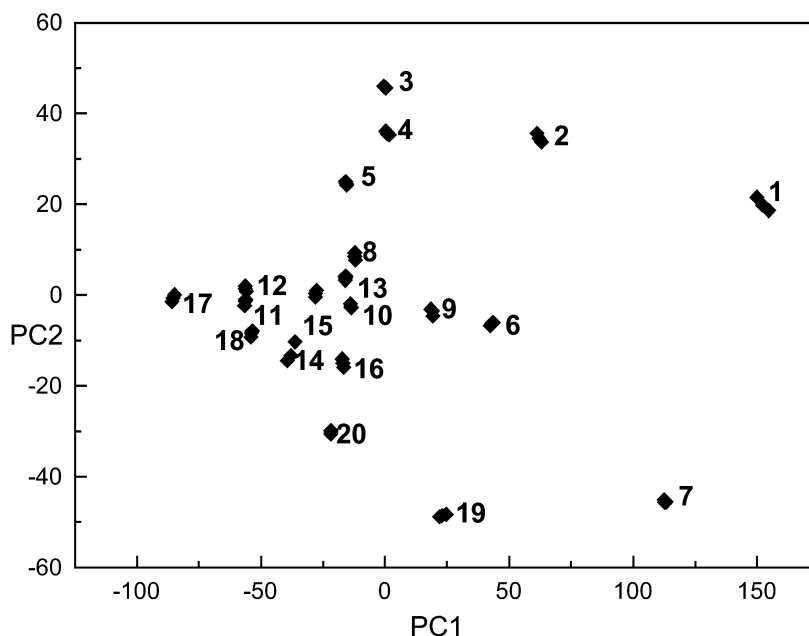
Fig. 7 Samples of B-type wine distinguished by using PCA. All 20 samples of wine of the same brand, very close in taste and chemical composition, are distinguished successfully by the electronic tongue.
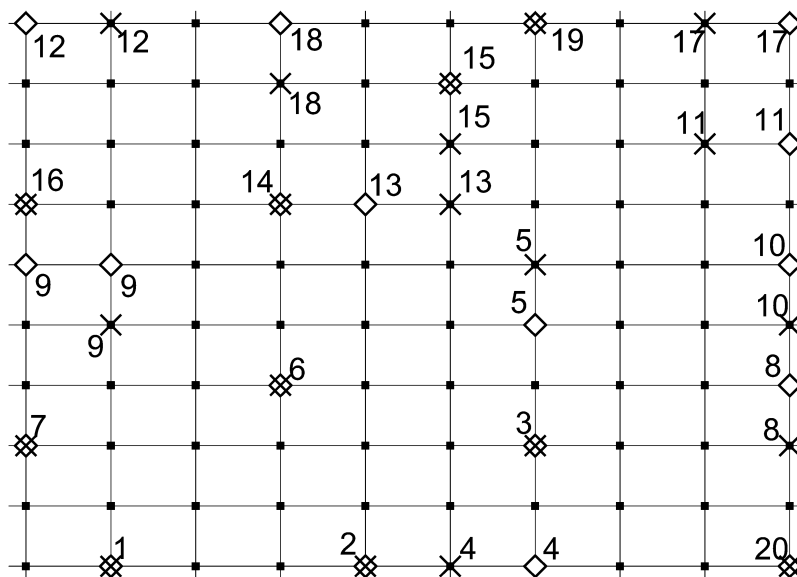
Fig. 8 The same B-type wine samples as in Fig. 4 distinguished by using SOM; ✕- calibration measurements, ◇- tests.

distances between points in the plot are proportional to the distances between classes in the classification model. In the SOM plot (Fig. 8), neurons are shown in fixed positions, although the distances between classes (winning neurons) are also different in reality.

In many practical applications, the class membership or sample identification has to be predicted. For that purpose, different classification models can be constructed by using supervised techniques, for

example, SIMCA based on PCA or the back-propagation neural network. For that purpose, the data have been split into two subsets, namely, one for calibration and validation of the model and the other for its testing.

8.2 Quantitative analysis

A very important field of application of the electronic tongue is quantitative determination of ions and neutral species in multispecies solutions. Principal advantages from application of the electronic tongue for quantitative analysis are:

(i)   determination of the concentration of ions in multispecies solutions, including ions for which no selective sensors are known. Results for the determination of ion concentrations in model ground waters are shown in the Table 2 [36].

(ii) higher selectivity and lower detection limit than for a single sensor.

Table 2 Concentrations of species in model groundwaters determined using the electronic tongue.

Species	Concentration actual /μmol dm^{-3}	Concentration found /μmol dm^{-3}	Standard deviation /μmol dm^{-3}
Cu^{II}	5.00×10^{-2}	5.00×10^{-2}	5.00×10^{-4}
	1.00×10^{-2}	1.00×10^{-2}	7.00×10^{-4}
Zn^{II}	1.0×10^{-2}	1.0×10^{-2}	7.00×10^{-3}
	0.50	0.51	0.05
	1.00	1.00	0.04
	1.00	1.10	0.1
Mn^{II}	5.0	5.6	2
	50	52	2
	1.00	1.00	0.03
Fe^{III}	5.00	5.00	0.09
	50	51	1
	50	51	1
Ca^{2+}	100	100	4
	1000	1000	70
	10 000	9900	300
Mg^{2+}	50	49	2
	100	100	7
	500	490	50
	1000	1000	10
	5000	4900	200
SO$_4^{2-}$	100	100	3
	1000	1000	70
	5000	5000	80
Na$^+$	200	200	7
	400	390	20
	2000	2000	100
Cl$^-$	300	300	7
	1200	1100	20
	40 000	42 000	1000

The electronic tongue can be calibrated by using different methods, the most typical being PLS and back-propagation neural network. PLS is a widely used method of multivariate calibration in chemical data processing [31–33]. ANN became popular in recent years (promising, but "hot and risky" [33]) and was also reported in relation to sensor arrays [35]. In some cases, ANN could be especially useful for processing significantly nonlinear data, but in many cases, both PLS and ANN methods should produce similar results. A neural network with one hidden layer and a hyperbolic tangent as the transfer function are used in the majority of calculation tasks.

For PLS, the data are split into two sets, that is, one for calibration and validation of the model and the other for its testing. Cross-validation should be used in order to construct a reliable calibration model. For ANN, the data have been split into three subsets, that is, one for calibration, the other for validation of the model, and the last one for its testing. Cross-validation must be performed in order to avoid ANN overtraining. The best network configuration chosen by using cross-validation is applied for evaluation of the test data. The calibration and test subsets have to be completely independent. Usually, the data obtained during the first days of an experimental session were used for calibration and validation, and the data obtained during the following days were used for tests.

The capabilities of both the PLS and ANN methods have been illustrated by means of an example in which the content of some organic substances, such as ethanol, organic acids, etc., were determined by using the electronic tongue [37]. The results of the determination of total acidity, the content of ethanol, (+)-tartaric acid [(2*R*,3*R*)-2,3-dihydroxybutanedioic acid] and shikimic acids [(3*R*,4*S*,5*R*)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid], as well as pH of the wine samples, are shown in Table 3 (data processed by PLS) and Table 4 (data processed by ANN) [26]. Comparing the results of quantitative analysis, one may conclude that the content of species in the wine, calculated by using PLS (Table 3) and ANN (Table 4), are not identical, but still very close to one another. The precision and error values obtained by using these methods are also comparable. Thus, both PLS and ANN can be used to process the results of the measurements performed with the use of the electronic tongue.

Table 3 Results of quantitative analysis of red Barbera wine samples using the electronic tongue. Data processing performed by PLS.

Wine sample	Alcohol actual vol. fraction/%	Alcohol found vol. fraction/%	Std. deviation vol. fraction/%	Mean error s/%*
1	12.7	13.3	0.2	5 %
8	13.4	13.58	0.08	1 %
6	12.79	12.9	0.1	1 %
16	12.08	13.1	0.1	8 %
	pH actual	pH found	Std. deviation	Mean error
2	3.47	3.42	0.01	1 %
3	3.52	3.49	0.01	1 %
4	3.42	3.46	0.01	1 %
	Tot. acidity actual/g L^{-1}	Tot. acidity found/g L^{-1}	Std. deviation/g L^{-1}	Mean error
1	9.83	8.65	0.09	12 %
11	9.68	9.32	0.01	4 %
12	9.38	9.53	0.03	2 %
13	9.00	9.84	0.02	9 %
14	10.20	8.27	0.05	19 %
	C(tart. ac.) actual/g L^{-1}	C(tart. ac.) found/g L^{-1}	Std. deviation/g L^{-1}	Mean error
1	4.41	4.37	0.04	1 %
12	4.17	4.10	0.03	2 %
13	3.5	3.92	0.02	12 %
14	3.73	4.02	0.07	8 %
	C(shik. ac.) actual/mg L^{-1}	C(shik ac.) found/mg L^{-1}	Std. deviation/mg L^{-1}	Mean error
2	27	33.3	0.4	23 %
6	28	39	2	41 %
19	17	15	2	10 %
20	37	24	2	36 %

Number of the sensors in the array, 29. Number of sensors considered during the data processing by PLS: for (+)-tartaric acid, shikimic acid, and total acidity, 14; for pH, 4. For each parameter, a separate calibration model was built by PLS. The number of species used in the calibration model: for tartaric acid, 10; for shikimic acid, 12; for total acidity, 9; for pH, 1.

*Mean relative error was calculated as

$$s = \frac{1}{n}\left[\sum_{i-1}^{n}\left(\frac{x-x_i}{x}\right)^2\right]^{1/2}$$

where n is the number of replicas, x is a reference concentration value used for calibration, x_i is the value predicted by the ET for the test set.

Table 4 Results of quantitative analysis of red Barbera wine samples using the electronic tongue. Data processing performed by ANN.

Wine sample	Alcohol actual vol. fraction/%	Alcohol found vol. fraction/%	Std. deviation vol. fraction/%	Mean error
1	12.70	12.74	0.01	1 %
6	12.79	12.40	0.02	3 %
8	13.40	12.01	0.02	10 %
16	12.08	12.24	0.01	1 %
	pH actual	pH found	Std. deviation	Mean error
2	3.47	3.54	0.01	2 %
3	3.52	3.59	0.01	2 %
4	3.42	3.59	0.01	5 %
	Tot. acidity actual/g L^{-1}	Tot. acidity found/g L^{-1}	Std. deviation/g L^{-1}	Mean error
1	9.83	9.81	0.01	1 %
12	9.38	10.55	0.01	12 %
13	9.00	9.23	0.01	3 %
14	10.20	9.36	0.05	8 %
	C(tart. ac.) actual/g L^{-1}	C(tart. ac) found/g L^{-1}	Std. deviation/g L^{-1}	Mean error
1	4.41	3.76	0.01	15 %
12	4.17	4.13	0.02	1 %
13	3.50	3.56	0.01	2 %
14	3.73	4.02	0.08	8 %
	C(shik. ac.) actual/mg L^{-1}	C(shik. ac.) found/mg L^{-1}	Std. deviation/mg L^{-1}	Mean error
2	27	34.4	0.1	27 %
6	28	31.9	0.2	14 %
19	17	29.2	0.2	72 %
20	37	38.8	0.2	5 %

Number of the sensors in the array: 29. Number of sensors considered during the data processing by ANN: 14 for all parameters. For each parameter, a separate calibration model was built by ANN.

Some other examples of quantitative application of the electronic tongue (data processed by PLS) are:

- heavy metal determination in polluted water (Table 2) [36];
- in situ determination of U(IV) and U(VI) in samples of mine water (Table 5) [38]; and
- determination of selected species in different mineral water samples (Table 6) [25,26].

Table 5 Concentration of uranium(VI), iron(II), and iron(III) in solutions modeling water in a flooded uranium mine, determined by using the electronic tongue.

Species	Concentration actual /mmol dm^{-3}	Concentration found /mmol dm^{-3}	Std. deviation /mmol dm^{-3}
Fe^{II}	0.10	0.21	0.04
Fe^{II}	1.0	1.6	0.2
Fe^{II}	5.0	4.3	0.4
Fe^{II}	10	8	1
Fe^{II}	100	100	6
Fe^{III}	0.1000	0.1000	0.001
Fe^{III}	1	1.4	0.6
Fe^{III}	5.0	4.8	0.5
Fe^{III}	10	18	9
Fe^{III}	100	100	5
UO$_2^{2+}$	1	3	1
UO$_2^{2+}$	16	26	7

Table 6 Results of quantitative analysis of mineral waters using the electronic tongue.

Water	Conductivity actual /μS cm^{-1}	Conductivity found /μS cm^{-1}	Std. deviation /μS cm^{-1}	Mean error s/%
Levissima	107.5	110	9	5
Fuiggi	156	155	1	6
Uliveto	1388	1414	69	4
Sangemini	1333	1302	204	14
Ferrarelle	1800	1792	120	5
SPellegrino	1306	1516	112	16
Tap	*	976	116	–
	Dry residual actual /g L^{-1}	Dry residual found /μS cm^{-1}	Std. deviation /μS cm^{-1}	Mean error s/%
Levissima	0.0735	0.075	0.006	8
Fuiggi	0.1065	0.105	0.002	2
Uliveto	0.986	1.03	0.05	5
Sangemini	0.9550	0.9	0.2	15
Ferrarelle	1.283	1.28	0.08	5
SPellegrino	1.109	1.10	0.09	6
Tap	*	0.70	0.08	–
	SiO$_2$ actual content /mg L^{-1}	SiO$_2$ found content /mg L^{-1}	Std. deviation /mg L^{-1}	Mean error s/%
Levissima	5.8	5.9	0.4	5
Fuiggi	18.80	19.7	0.6	5
Uliveto	7.0	7.1	0.2	3
Sangemini	24.50	22	2	10
Ferrarelle	83	85	7	7
SPellegrino	9	7.9	0.5	12
Tap	*	55	7	–

*For tap water, quantitative analysis results are not available.

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

a_i	activity in solution of ion i
ANN	artificial neural network
E	potential difference between working and reference electrodes
$E°$	standard potential
F	Faraday constant
gasFET	gas-sensitive field-effect transistor
immunoFET	immunoassay field-effect transistor
ISE	ion-selective electrode
ISFET	ion-selective field-effect transistor
$K_{i,j}$	selectivity coefficient of ion i against ion j
opt(r)ode	optical sensor
PARC	pattern recognition
PC1	principal component 1
PC2	principal component 2
PCA	principal component analysis
PLS	partial least-squares regression
PVC	poly(vinyl chloride) [poly(1-chloroethylene)]
R	gas constant
SIMCA	soft independent modeling of class analogy
SOM	self-organizing map
T	thermodynamic temperature
z_i	charge number of ion i

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