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ORIGINAL PAPER

An electronic tongue for qualitative and quantitative analyses of anions in natural waters

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Abstract Based on the cross-sensitivity shown by certain metal electrodes for some anions in a liquid media, an array of five potentiometric electrodes (Au, Ag, Pt, Cu and Zn) has been used as an electronic tongue device for the recognition and prediction of common anions chloride, sulfate and bicarbonate in mineral waters. The recognition testing studies included measurements of potential (emf) on solutions of pure salts, mixtures of salt and some mineral waters. Predictions were performed by using partial least square. A good discrimination between different water samples by PCA analysis was found as well as an adequate prediction of the concentration of chloride and sulfate.

Keywords Electronic tongue · Potentiometry · Multivariate analysis · Prediction model

1 Introduction

As an attempt to reproduce artificial human sensory reception, scientists have been working for years in the development of devices capable of emulating this human ability. At the beginning of the eighties Persaud and Dodd [1] created the first electronic system (called electronic nose) for gas recognition that by some means worked in a similar way as the human sense of smell does. Since then, a high number of works have been devoted to the development of electronic noses [2–5]. Lately, the concept was translated to the human sense of taste and electronic tongues (or taste sensors) were created [6, 7]. Today this widely used term refers to an array of non-specific sensors that combined with pattern recognition techniques and/or multivariate calibration of data allows getting information from complex solutions. In both electronic nose and tongue approach, the key concept relies on the use of a set of “sensors” that respond rather unspecifically but in some way differentially toward a group of related chemical species. Thus, the main objective when designing electronic tongues is not to measure single specific chemical components in a highly selective manner but usually to get images of more general “human” attributes such as taste, quality, etc. Field of application of electronic tongues involve food industry analyses [8–10], medical/pharmaceutical evaluations [11, 12] and environmental monitoring [13, 14], among others.

The design of electronic tongue devices has been carried out following the use of either potentiometric, voltammetric, optical or piezoelectric sensor arrays. Voltammetry has been reported to show several advantages related with the versatility and robustness of the voltammetric methods [15]. Among different techniques, pulse voltammetry has been mainly used to get information from multi-component solutions [16, 17]. In potentiometric techniques, the potential between two electrodes when there is no current flow is measured. Several examples of potentiometric electronic tongues have been reported [18–20], most of them having in common the use of membrane potentiometric sensors. The membranes can be of different materials including chalcogenide glass sensors [21], PVC, or lipid/polymer membrane electrodes [22], Langmuir–Blodgett membranes [23], etc.

Following a rather different approach we have recently reported the use of certain simple electrodes such as metal-

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based electrodes of the M/MO/OH$^-$ or M/MX/X type, as a set of very unspecific and undemanding potentiometric sensors. These surfaces display a very cross-sensitive response but still differentiable toward a group of chemical species. Specifically we have used this approach for the differentiation of water samples [20] and as electronic tongues for fish quality monitoring [24]. The specific case of discrimination or differentiation of natural water is very demanding because the only difference between water samples is usually the presence of compulsory water anions and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, and $HCO_3{}^-$) typically in a not very wide range of concentrations. Thus, for instance, a great effort has been devoted to the preparation and synthesis of receptors for anions [25]. Additionally, some of them have been incorporated into membranes for the development of ion-selective electrodes or have been functionalized with dyes for the preparation of functional receptors for the optical (colorimetric or fluorimetric) determination of anions [26, 27]. However, a usual drawback associated to anion receptors is related with the fact that many ligands display sensing features in organic solvent but not in pure water due to competitive water interaction with the anion that significantly reduces the anion interaction with the guest. The possibility of using electronic tongues for the quantitative or semi-quantitative prediction of concentrations of anions in water is very appealing and simple especially when compared with the highly demanding synthetic efforts needed to prepare abiotic anion receptors for the development of anion sensors. In our previous work, we demonstrated that a set of metal-based non-coated surfaces could be successfully employed for the differentiation of rather similar water samples (e.g. identification success rate was higher than 93%). In this paper we took a step further and it was our aim to study the possible use of very simple systems for quantification. Therefore, we report herein an electronic tongue that is able to roughly predict the concentrations of anions in natural water samples using an array of five potentiometric metal-based wires (Au, Ag, Pt, Cu and Zn) and a conductivity electrode.

2 Experimental

2.1 Preparation of the E-tongue

The set of the five potentiometric metal-based electrodes (Au, Ag, Pt, Cu and Zn) was prepared as follows: a wire of each metal (1.0 mm diameter, >99.9% purity, purchased by Aldrich) was introduced and encapsulated into a stainless steel cylinder used as electrode body. Before using, the electrodes were cleaned both mechanically and chemically with an emery paper and rinsed with ethanol and distilled water. Before immersing in the samples, the electronic tongue was polished with an electrical device, ensuring the re-generation of the sensors surface. Using an additional electrode the conductivity of the solutions was also measured.

2.2 Samples

Three types of samples were used for qualitative analysis, namely pure salt solutions, mixtures of salts and mineral waters. In the first case, solutions of KCl, K_2SO_4, $KHCO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ were prepared both buffered and non-buffered. The buffered samples were prepared by using the corresponding salt into a 10^{-2} molar solution of *N*-[2-hydroxyethyl] piperazine]-*N*′-[2-ethanesulfonic] acid (HEPES) as buffer, and adjusting the pH to 7.0 with NaOH or HNO_3. Salts of two different cations (Na^+, K^+) were used in order to asses the cation effect in the detection of the anionic species. The concentration of all prepared pure salt solution samples was 0.05 mol dm^{-3}. In the case of mixtures, three samples namely M1, M2 and M3 were prepared by mixing the corresponding buffered solutions of KCl, K_2SO_4 or $KHCO_3$. The final composition of the mixtures is shown in Table 1.

Eight samples of mineral waters purchased by a local market in Valencia were also analyzed in this study. The samples were purchased according to their chemical composition (including Cl^-, $SO_4{}^{2-}$ and $HCO_3{}^-$ as principal anionic components). Hence, waters of "very low mineralization" (i.e. Bezoya and Montcalm), "low mineralization" (i.e. FontVella, Lanjarón) and some sparkling water with high content of bicarbonate (i.e. Primavera, Perrier,

Table 1 Anionic composition (mol dm^{-3}||g dm^{-3}) of mixtures

	Cl^-	$SO_4{}^{2-}$	$HCO_3{}^-$
M1	0.03||1.06	0.015||1.44	0.005||0.31
M2	0.005||0.18	0.03||2.88	0.015||0.91
M3	0.015||0.53	0.005||0.48	0.03||1.83

Table 2 Chemical composition of mineral waters (mg dm^{-3})

	$HCO_3{}^-$	Cl^-	$SO_4{}^{2-}$	Ca^{2+}	Na^+	Mg^{2+}
Bezoya	18	<1	–	4	1	2
Montcalm	5.2	0.6	8.7	3	1.5	0.6
FontVella	149	16.2	16.8	38.5	13.2	9.7
Lanjarón	105	–	17.3	27.2	4.8	8.8
Primavera	297.2	35.8	43.9	88.7	18.6	23.4
Primavera gas	297.2	35.8	43.9	88.7	18.6	23.4
Perrier	420	23	42	149	11.5	7
VichyCatalan	2081	584	49.6	–	1097	–

VichyCatalan) were selected. The chemical composition of the mineral waters used is shown in Table 2.

Quantitative analyses were carried out in order to verify the capability of the potentiometric electronic tongue for determining anionic content in aqueous solutions. For this purpose, PLS prediction models were built in the first step, followed by validation of the created models. For creating PLS models, a calibration which includes measurements on standard solutions is necessary. By using an experimental design software (MODDE 8.0) a total of 18 standard solutions was determined. The solutions (composed by anions chloride, sulfate and bicarbonate) were prepared following a similar procedure as for M1, M2 and M3 but with levels low (0), medium (0.015 mol dm^{-3}) and high (0.03 mol dm^{-3}). The concentration of each anion on the samples was established by using the MODDE 8.0 software. The validation of the created predictor models was carried out by measuring and predicting the anionic content in samples with unknown concentration of studied anions. For this purpose, some samples were selected, i.e. mineral waters Bezoya, Lanjarón and FontVella (used previously in the qualitative analysis), also tap water (from Valencia) and a sample from the Mediterranean Sea (beach “La Malvarrosa” in Valencia). The samples were buffered as described earlier. The sea sample was filtered to remove solid particles.

2.3 Measurements

Three measurements of the electrode potential versus Ag/AgCl reference electrode for each sample were collected. Each simple measurement gives 200 values of potential (one value every 1 s during 200 s). This means 1000 values of potential (for all the five electrodes) on each sample. All measurements were taken using the OPA129P operational amplifier with high input impedance (10^{15} Ω) configured as tension buffer and a data acquisition card ADLINK-9112 using a program developed with LabView. The resolution of the acquisition of measurements is ±0.6 mV. Simultaneous measurements of conductivity (Crison GLP 32) and pH (for non-buffered samples) (Crison GLP 22) were also performed.

2.4 Data management: multivariate analysis

Multivariate analysis was used to treat all data collected from the experiment, specifically principal component analysis (PCA) (qualitative analysis) and partial least square (PLS) (quantitative analysis). The main objective of PCA is reducing the data set to lower dimensions, or less quantity of variables (also namely principal components). The aim of PLS is to predict Y from X, by simultaneous decomposition of those matrixes or vectors in a group of components (latent variables) which explain as much as possible the covariance of X and Y [28]. Prediction models are built by using the calibration set (standard solutions) and the collected data from the sensors. Prior to building up the model, cross validation was used to evaluate the adequacy of the experimental data, and for selecting the quantity of latent variables. Standardization of the data is also performed by an auto scaling of the emf/conductivity data (X matrix) and also the levels (Y matrix) to mean zero unit variance. All data management was carried out with Matlab (Version R2006b, MathWorks).

3 Results and discussion

3.1 Qualitative analysis: recognition of anions

The general idea in the use of metal electrodes is based on the fact that many types of surfaces might be polarized in aqueous environments due to either physisorption or chemisorption processes of a number of chemical species. This spontaneous polarization (which is known to be very dependent on the chemical characteristics of the electrode surface), however, is a quite unspecific process and this is why non-coated or non-modified conducting active surfaces are not used as selective sensors. Nevertheless, it is precisely this unspecificity, and therefore the large cross-sensitivity, that can be an appealing characteristic for the development of electronic tongues. The use of rather unspecific conducting surfaces might be a promising sensing approach due to the large number of available possibilities to tune the composition of the final sensor array which might turn in controlling the response to different complex liquid mixtures.

After a number of attempts, using different metallic electrodes and a combination of them, the final electronic tongue selected for this study consisted of wires (1 mm diameter) of five metals (Au, Ag, Pt, Cu and Zn) that were encapsulated into a stainless steel cylinder. Prior to the use of the set of electrodes these are polished with an electrical device in order to ensure the re-generation of the sensors surface. As an additional data the conductivity of the prepared solutions was also measured.

It was our aim to prepare an electronic tongue able to distinguish between similar natural waters by their anionic content. Natural waters contain mainly the anions HCO_3^-, Cl^- and SO_4^{2-}. Therefore, all the following studies were carried out using a mixture of these anionic species. In a first experiment, different solutions containing $KHCO_3$, $NaHCO_3$, NaCl, KCl, Na_2SO_4 or K_2SO_4 were studied. Three measurements of the electrode potential versus Ag/AgCl reference electrode for each sample were collected. Each simple measurement gives 200 values of potential (one value every 1 s during 200 s). This means 1000 values of potential (for all the five electrodes) on each sample. In order to analyze the possible existence of recognition patterns in the emf variation, PCA was used (see Fig. 1). PCA involves a mathematical procedure that transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components (PC). The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. Figure 1 shows the PCA plot for the data matrix including both emf data and conductivity of buffered solutions of the corresponding salt. As it can be seen the different samples appear well separated and there exists a pattern mainly governed by the presence of anions, although a cation separation can also be observed. Separation by cations is fundamentally observed for samples of chloride and sulfate salts. The cluster of chloride salts locates in the zone of more negative values of the first component PC1 axis meanwhile the sulfate clusters appear in the highest values of PC1. Samples with anion bicarbonate appear in the 0 value of PC1 and in the more positive values of PC2, although PC2 only explain 31% of variance of data.

In a further experiment, measurements of the emf and conductivity for the mixtures M1, M2 and M3 (prepared by mixing of pure buffered solutions of KCl, K_2SO_4, $KHCO_3$ in a ratio 6:3:1, see Table 1) were carried out. With these new data a matrix was created containing both the measurements obtained from the M1, M2 and M3 mixtures and also data of the respective pure sample KCl, K_2SO_4 and $KHCO_3$. Three independent measurements for each sample were performed. In the PCA plot (Fig. 2), the clusters of both types of samples (pure solutions and mixtures) are well separated, clearly indicating the existence of a recognition pattern based not only by the presence of anions but also in the differences of anion concentration. The pattern can be found by simple observation of the position of clusters in the PCA plot. Hence, drawing an imaginary triangle with vertex in the center of the cluster of each pure salt sample, we can observe a clear relation between the composition of each mixture and its position in relation to the pure salt. For instance, the M2 sample is located close to the vertex of K_2SO_4 and far from vertex of KCl (M2 composition: 0.03 mol dm^{-3} K_2SO_4, 0.015 mol dm^{-3} $KHCO_3$, and 0.005 mol dm^{-3} KCl). A similar effect is observed for M3 that is very close to the position where pure $KHCO_3$ samples lay (M3 composition: 0.005 mol dm^{-3} K_2SO_4, 0.03 mol dm^{-3} $KHCO_3$, and 0.015 mol dm^{-3} KCl). A close upshot was found for sample M1 that contains a higher concentration of chloride. On the other hand, the percent of variance of each PC can be related with the levels of the species according with the clusters location. Herein, in the PC1 axis, higher concentrations of chloride are located in negative values of PC1 meanwhile lower concentrations are located in positive values. The contrary occurs for sulfate, locating the highest concentrations in the positive values of PC1. In the case of bicarbonate, the second component PC2 explain better the differences of levels of this anion, locating the highest concentration at positive values.

In further experiments, a more practical verification of the recognition pattern based on the species concentration is performed. Data collected from measurements of emf on eight mineral waters were analyzed. The samples have in common the presence of anions SO_4^{2-}, Cl^- and HCO_3^- and some alkaline and alkaline earth cations (see Table 2). PCA plots include data of emf and conductivity for mineral waters and also for the mixtures M1, M2 and M3. The measurements were taken immediately after opening the

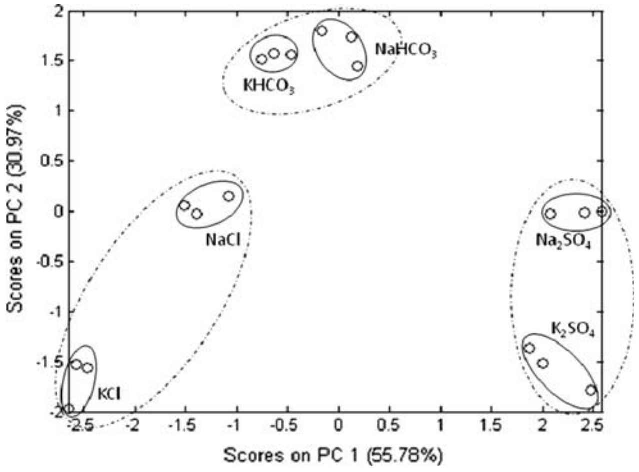

Fig. 1 PCA plot of buffered salt solutions of potassium and sodium (emf and conductivity)

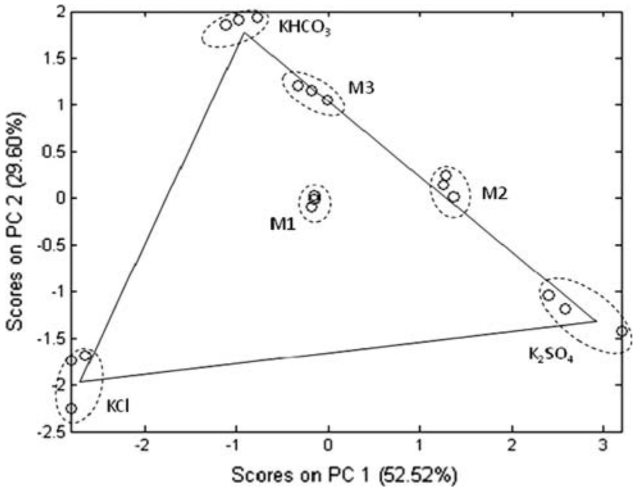

Fig. 2 PCA plot of buffered mixtures M1, M2 and M3 and corresponding pure salt solutions (emf and conductivity)

bottles. In the PCA plot, four well-defined zones of clusters location can be observed (see Fig. 3). One zone corresponds to the positive quadrant (PC1; PC2) in which the samples Bezoya and MontCalm with a "very weak mineralization" are located. In a central zone are clustered the samples of FontVella and Lanjarón with "weak mineralization" and also Primavera, with a mineralization slightly higher. Sparkly waters appear well separated from the rest, in the zone of minimum (negative) variance of PC2. Here, Perrier and Primavera-gas are located very closely, while VichyCatalan is located separately from the rest (toward minimum value of PC1) most likely due to its very high ionic content (mainly bicarbonate). It is important to note that the two PC explain about the 91.6% of the date variance (66.38% PC1 and 25.3% PC2).

The position of the mixtures M1, M2, M3, and also VichyCatalan (samples with the highest ionic content) in the zone of minimum variance of PC1 and contrary, the position of Bezolla-Montcalm (samples with the lowest ionic content) in the PC1 positive zone, indicates the existence of certain correlation between first component PC1 and the ionic concentration in the samples.

A similar classification of mineral waters has recently been reported by us [20]. Moreover, potentiometric electronic tongues for water analysis using a more complex array of chemical sensors have also been reported. For instance, Legin et al. have described an electronic tongue comprising 29 potentiometric chemical sensors, including sensors with calcogenide glass and PVC membranes, that was used for the analysis of Italian produced mineral waters [29]. Also, an array containing 22 chalcogenide glass electrodes has been applied by Natale's group to the study of waste waters [30]. Bratov et al. have described the use of a monolithically integrated array of ion selective field effect transistors (ISFETs) of K^+, Na^+, Ca^{+2} and Cl^- for mineral water analysis [31]. It is also noteworthy that apart from the use of potentiometric tongues, voltammetric tongues have also been applied to the analysis of waters, for instance, from the paper mill industry [32] and drinking water [33].

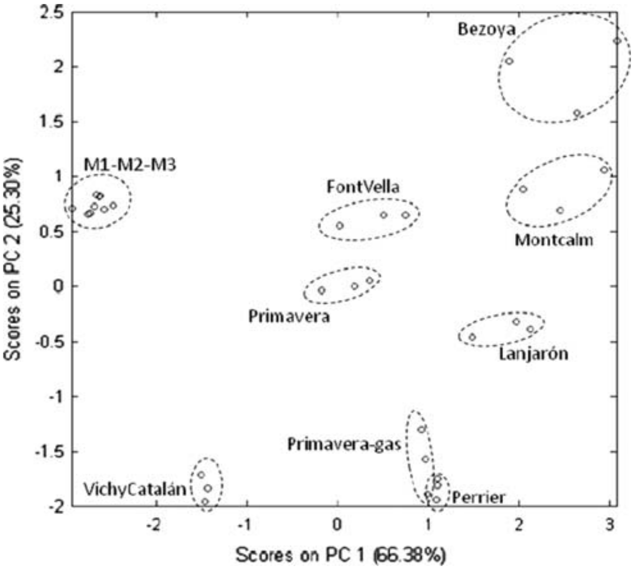

Fig. 3 PCA plot of mineral waters and mixtures (emf and conductivity)

3.2 Quantitative analysis: prediction of anionic levels

Following the recognition pattern based on metal-assisted anion recognition verified in the previous section, prediction models were created here by using PLS, in order to study the possible use of a simple set of metal to determine anion concentrations in water samples. To build the model, it is necessary first to make training by using a calibration set composed by standard solutions of anions. The training was performed by measurements of emf in 18 standard solutions (containing anions chloride, sulfate and bicarbonate) that were prepared following a similar procedure as for M1, M2 and M3 but with levels low (0.0 mol dm^{-3}), medium (0.015 mol dm^{-3}) and high (0.03 mol dm^{-3}). The concentration of each anion on the samples was established by using the MODDE 8.0 software. Three measurements were carried out on each solution; each measurement includes 200 values of emf for each electrode. Additionally, all the samples were measured in a random order to avoid possible time-dependence effects on the potentiometric measurements. The conductivity of standard solutions was measured as well. After the measurement procedure, all the data were cross-validated to check the adequacy of the data, and also to extract the appropriate number of latent variables to create PLS prediction models.

Prediction models were created for each species. Results of the prediction are displayed in the PLS plot scores, which represent the correlation between predicted and measured values (measured values are the known concentration of each species on each standard solution). The adequacy of the created prediction model can be evaluated by a fitting of the data. Thus, by using a linear model fitting $y = p1 * x + p2$, coefficients $p1$ and $p2$ are obtained, as well as the term *norm of residuals*, which is related with the precision of the model. In terms of accuracy, coefficient $p1$ (slope of the fitting curve) can be considered as an index of it.

The plot of predicted versus measured values for anion chloride is shown in Fig. 4. The prediction of the concentration of chloride is much more accurate than the rest of anions, according to the lowest spread of experimental points along the straight line of levels, and also by the best fitting in terms of a highest/closest-to-one value of coefficient $p1$ and the lowest value of norm of residuals.

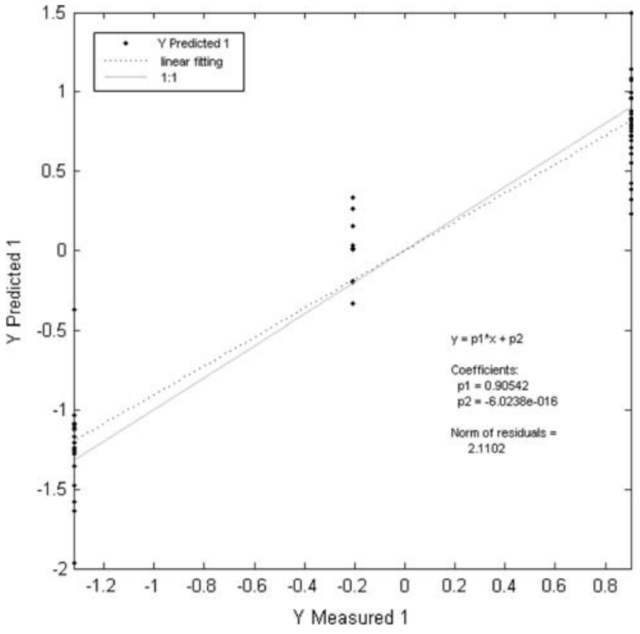

Fig. 4 Plot score of prediction model of chloride for the calibration set

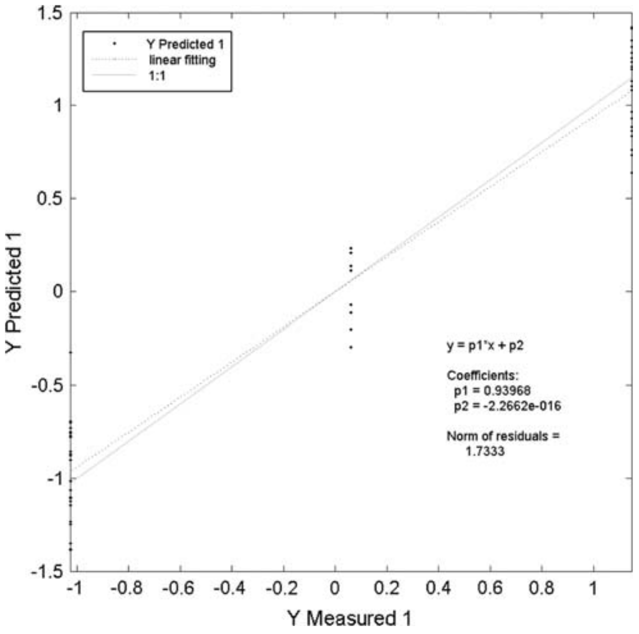

Fig. 5 Plot score of prediction model of sulfate for the calibration set (including conductivity measurements)

Prediction of both bicarbonate and sulfate can be considered moderate compared with results on chloride (bicarbonate and sulfate exhibited values of slope/norm of residuals of 0.685/3.38 and 0.644/3.48 respectively).

At this point, it is important to remark the changes observed in the result by including the conductivity of the solutions as a variable into the data matrices *X*. The prediction of bicarbonate does not exhibit a noticeable change (values of slope and norm of residuals are similar 0.689/3.37) by inclusion of the conductivity. On the contrary, the prediction for sulfate improves remarkably, with an increasing of the precision (referred to a diminishing of norm of residuals) from 3.48 to 1.73 and a higher accuracy related to a slope of 0.94 (see Fig. 5). This behavior is reasonable taking into account that the molar ionic conductivity of sulfate ($\lambda^0 = 160\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) is remarkably higher than for ions chloride ($\lambda^0 = 76.3\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$) and bicarbonate ($\lambda^0 = 44.5\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$).

Validation of prediction model is performed by measuring emf and conductivity and subsequent calculations of predicted levels in samples not included in the calibration process. Calculations are performed over the new data matrix by using the PLS model built previously on the calibration set. Herein, samples with remarkable differences in anionic levels have been chosen for this analysis, namely mineral waters Bezoya, FontVella and Lanjarón, as well as tap water (from Valencia) and seawater (from Valencia) (see Sect. 2). Table 3 shows the levels of anions of each sample, as well as the numerical results of predictions. The concentrations of studied anions in mineral waters are obtained from the composition information in the bottle label; meanwhile the anionic content of both tap water and the sea sample were determined by an analysis of anions in waters and seawaters [34, 35]. Results of validation of the electronic tongue show a predicting ability for the determination of the concentrations of anions chloride and sulfate more accurate than for bicarbonate as expected according to the previous results in the calibration. These predictive capabilities for chloride and sulfate can be considered as moderate in terms of accuracy. Nevertheless,

Table 3 Comparison between predicted and real concentrations of chloride, sulfate and bicarbonate in water samples

Sample	Predicted concentration (mg dm^{-3})			Real concentration (mg dm^{-3})		
	Cl^-	SO_4^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	HCO_3^-
Bezoya	4.8	–	29.4	<1	–	18
Tap water	89.7	240	474	117	286	251
Lanjarón	3.08	7.4	198	–	17.3	105
Font Vella	24.6	22.2	312	16.2	16.8	149

it is noteworthy that, as far as we know, this is the first time that a simple set of metallic electrodes is used for the determination of anion concentrations in water. We believe that this or similar electronic systems might be suitable for the semi-quantitative prediction of anion concentrations in water samples for certain applications. Predictions in the seawater sample (not included in Table 1) are completely imprecise which is ascribable owing to two reasons: the levels of anions are much higher than the levels in standard solutions used in the calibration; and the presence of a high number of other active and non-active species in the seawater which can affect the response of the sensors (matrix effect).

4 Conclusions

An electronic tongue based on five potentiometric metal-based electrodes has been designed. This electronic tongue is capable of distinguishing solutions with different anionic contents, following a recognition pattern based on the cross-sensitivity of the metallic electrodes toward anions. Certain affinity of the electrodes for the alcaline cations was observed as well, although the affectation to the discrimination/separation of anions is minimum. The existence of a recognition or separation pattern in terms of differences in levels of anions in the samples has been also found and verified. The electronic tongue made from metallic electrodes has been used for the first time for the prediction of concentrations of anions in water. A reasonable determination in the concentration of chloride and sulphate was found, whereas the determination of bicarbonate is less accurate. Further studies are being carried out in order to apply this or similar electronic tongues for the semi-quantitative determination of anion concentrations in selected applications.

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