



Multicomponent analysis of drinking water by a voltammetric electronic tongue

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ABSTRACT

A voltammetric electronic tongue is described that was used for multicomponent analysis of drinking water. Measurements were performed on drinking water from a tap and injections of the compounds NaCl, NaN_3 , NaHSO_3 , ascorbic acid, NaOCl and yeast suspensions could be identified by use of principal component analysis (PCA). A model based on partial least square (PLS) was developed for the simultaneously prediction of identification and concentration of the compounds NaCl, NaHSO_3 and NaOCl. By utilizing this type of non-selective sensor technique for water quality surveillance, it will be feasible to detect a plurality of events without the need of a specific sensor for each type of event.

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1. Introduction

There is a growing awareness of the importance of drinking water as a crucial part of the infrastructure of a nation. Drinking water plays an essential role in today's society, not only for drinking purposes, but also for sanitary reasons, household white-ware and for many industrial processes, especially in the food sector.

Drinking water is normally taken from surface or ground water and treated in a drinking water production plant. The raw water is then often first chemically precipitated to remove color and particles and thereafter passed through a number of sand filters, where the water is biologically cleared from bacteria and odors. Finally acid/alkali and sodium hypochlorite are added to adjust pH and to disinfect. Due to origin and quality of the raw water, the quality of the produced drinking water may normally vary slightly. Disturbances of the quality of the raw water may be due to high amounts of algae, other microorganisms or industrial contaminants. If the raw water is treated properly in the drinking water production plant, these disturbances do normally not constitute a health risk, although the drinking water may have an unpleasant odor and/or taste. Accidents have, however, occurred; due to unsatisfactory purification of raw water containing the pathogenic microorganism *Cryptosporidium*, contaminated drinking water was distributed at several occasions in Ireland during the years 2000–2007, in one occasion causing over 200 people to get sick.

If the pipes distributing the drinking water to the consumer have an inner coating that is partly removed due to e.g. a temporary high flowrate, the drinking water may be discolored, sometimes also followed by unpleasant taste, although in most cases not harmful to the health. The produced drinking water may also be contaminated if mixed with water from an external source. This might be due to natural causes such as an effect of flooding due to heavy rain showers, accidents or by purpose (e.g. terrorist activities). A severe case is if sewage water is mixed with drinking water, due to the content of pathogenic bacteria. This had e.g. occurred in the city of Boden, Sweden in 1993, and in the city of Nokia, Finland in 2008. In Camelford, Great Britain, large levels of alumina sulphate was accidentally added to the drinking water in 1998 [1], leading to nausea, vomiting and other symptoms, and in 2001, ammonia was spilled into the main waterline in Tel Aviv, Israel, causing high pH and turbidity levels in the drinking water [2].

Due to the growing awareness of sustaining good quality of the drinking water, the interest for monitoring systems has accordingly increased. For example, at Linköping University, Sweden, a specially designed project, EVENT, was initiated in 2008 aiming at strengthening and developing existing crisis management systems with the focus on water quality monitoring [3]. In this project, a sensor network will be incorporated in a test version of a small part of a municipal drinking water system for detection of unexpected events due to biological and/or chemical substances. The sensor system is connected to the municipal crisis management system, which will lead to faster actions if e.g. terrorist attacks, sabotage, accidents or contamination due to natural causes occur. Since this monitoring system will potentially cover a large deal of the municipal drinking water system, a large number of sensors

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will be needed. This means that the sensors used must be simple, cheap and robust.

Several sensor technologies can be used for drinking water monitoring. There are commercial sensors on the market for a number of compounds, important for water quality monitoring. These include measurements of temperature, specific conductivity, pH, free chlorine, oxidation–reduction potential (ORP) dissolved oxygen, turbidity, total organic carbon (TOC), chloride, ammonia and nitrate. In an investigation [4], all these sensors were mounted in a recirculation loop and subjected to various contaminants such as insecticides, potassium cyanide, nicotine, arsenic trioxide, aldicarb and *E. coli* K-12 strain with growth media. The sensors that responded to most contaminants were those that measured free chlorine, TOC, ORP specific conductivity and chloride. Introducing these kind of sensor systems to a drinking water pipe is, however, complicated, expensive and labor-intensive, and only used by large industries.

The concept of the electronic tongue might in this respect be very useful. These types of systems, together with “Electronic nose”, are the so called biomimetic system, since they use Nature as a model, thus functioning in a similar way. They are based on arrays of semi-specific sensors that produces a signal pattern when subjected to a sample, that can be related to either a specific compound or a quality aspect, which is done by treating the signal pattern with multivariate data analysis (MVDA). In a diagram, each set of a signal pattern can be represented by a single point, and signal patterns related to each other will form clusters. Thus, various signal patterns can be correlated to a compound or a quality aspect. Furthermore, by using a set of signal patterns as training set, a model can be calculated to be used for prediction of unknown samples.

The first electronic tongues described were based on arrays of potentiometric ion selective electrodes and mainly used for quality assessments of drinks [5–7] and to follow river pollutions by heavy metals [8]. Electronic tongues based on voltammetry, in which ionic and redox active compounds are measured have also been developed [9–11]. Potential pulses of different sizes are then applied to a working electrode and the resulting current pulses are then a measure of ionic and redox active compounds. When using voltammetry in complex media, rather complicated current spectra are obtained and the interpretation of data may be difficult. Still, these voltammograms contain a large amount of information and to extract this information, multivariate calibration methods have been shown to be very valuable [12,13].

Compounds of interest for water quality estimations that can be measured using a voltammetric electronic tongue are e.g. dissolved oxygen, oxidation–reduction potential (ORP), sodium hypochlorite (used as disinfectant in drinking water), total and free chlorine, hydrogen peroxide and many more. Due to how the potential pulses are applied to the working electrode, also other types of parameters can be measured. It has thus been shown that pH, conductivity and chemical oxygen demand (COD) could be measured [14] as well as bacteria content in process water [15]. In other studies using the technique estimations of drinking water quality [10,11], classification of detergents [16,17] and measurement of heavy metals [18,19] have been performed.

There are several advantages of using voltammetric electronic tongues for drinking water monitoring. Apart from being very robust and able to measure a very large amount of different compounds, the very concept of the multivariate approach applied to a voltammetric electronic tongue reduces the need of a reference electrode.

In this article, it is shown how a voltammetric electronic tongue can be used for multicomponent analysis of drinking water. An MVDA based model could be developed for the simultaneous prediction of both identity and concentration of the compounds NaCl, NaHSO₃ and NaOCl. By utilizing this type of non-selective sensor

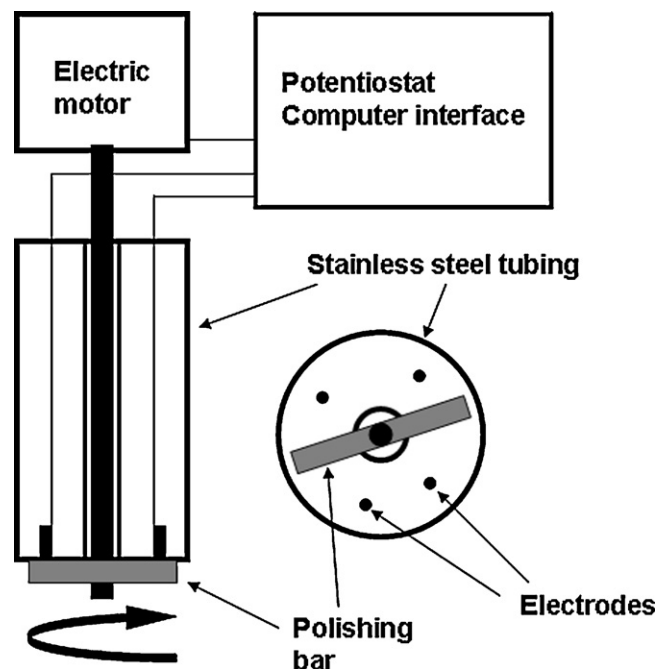


Fig. 1. A schematic illustration of the voltammetric electronic tongue.

technique for the EVENT project, it will be feasible to detect a plurality of events without the need of a specific sensor for each type of event.

2. Experimental

2.1. Chemicals

The chemicals NaCl, NaN₃, NaHSO₃ and ascorbic acid were all of analytical grade. NaOCl was obtained as a 30% solution. Dry yeast (1 g) was dissolved in 200 mL of drinking water and stirred for 30 min before use.

2.2. The electronic tongue

The voltammetric electronic tongue, schematically shown in Fig. 1, contained four working electrodes of gold, iridium, platinum and rhodium. The materials of the working electrodes have been chosen to optimize different catalytic properties and to have long-term stability, thus noble and catalytic metals are used. These choices of metals as working electrodes in the voltammetric electronic tongue (VET) have been standard since more than a decade (in some cases, however, the iridium electrode has been replaced by an electrode of stainless steel). Due to the different catalytic properties of each metal, each working electrode will produce a unique signal pattern.

The working electrodes (diameter 1 mm) were placed in a stainless tube (length 100 mm, diameter 40 mm) and embedded in a dental material (Filtec, The 3M Company, USA). The stainless steel tubing served as counter electrode. The VET was also equipped with a polishing unit, consisting of a wet-sandpaper strip (mesh 1200) that was slightly pressed and rotated via a rod against the electrode surface. At the other end, the rod was connected to an electrical motor. It was also equipped with a positioning unit. The beauty of the self-polishing unit is that after each polishing step, a brand new electrode surface is generated. This means that the system will have excellent long term and stability properties, and is in principle maintenance free [11].

The set-up, including the voltammetric electronic tongue, is schematically shown in Fig. 1.

Current transient responses were measured by a potentiostat connected to a PC via an A/D–D/A converter. The PC was also used for onset of pulses and to store data. The voltammograms recorded were based on large amplitude pulse voltammetry (LAPV). A measurement sequence was started by applying a potential of -300 mV during 50 ms. The voltage was then set to 0 during 50 ms, where after the applied potential is increased by 100 mV, and the process was repeated until a potential of $+800$ mV was reached, resulting in a total of 22 pulses. The sampling rate was set to 200 Hz, thus 10 measurement points were collected for each voltage interval, and the first, second and tenth sample in each interval were stored. Each electrode was thus described by 72 datapoints, hence, a total measurement sequence is given by 288 datapoints. A polishing sequence was initiated after each fourth measurement sequence, and only the last measurement sequence was used for data processing. Measurement data could be collected each fifth minute. Due to the onset of a voltage pulse, a sharp current pulse is generated when charged species (with opposite charges) in the solution are attracted to the electrode and form a so called Helmholtz layer and that redox active compounds near the electrode surface will be oxidized or reduced. The current will then decay and reach an equilibrium when the Helmholtz layer is completely formed, as shown in Fig. 3, and given by the concentration of redoxactive substances present and their diffusion coefficients. Thus, the height of the initial current pulse is then given by the sum of electroactive species (corresponding to the conductivity of the solution) and the concentration of redoxactive species. The current will then decay and reach an equilibrium when the Helmholtz layer is fully formed, as shown in Fig. 2, given by the concentration of redoxactive substances present.

If no redox active compounds are present, the current will go to zero. When the voltage is turned off, similar current responses will be obtained, but with opposite directions. Studies of the transient responses may give information concerning diffusion coefficients of charged species. Due to the short pulse length (50 ms) in the experiment described, equilibrium will not be reached. The initial part of the current response is most correlated to the conductivity of the solution, and the equilibrated part is mainly correlated to the presence of redox active compounds.

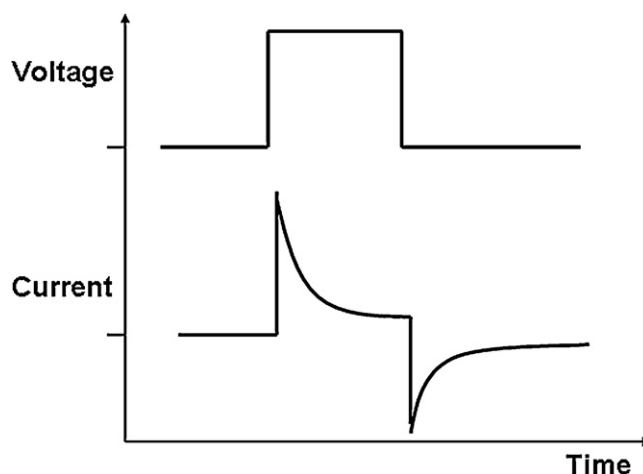


Fig. 2. Sharp current pulses are generated due to onset and end of a voltage pulse. The steady state current is the redox (or faradic) current at the potential of the electrode.

The surface of the counter electrode is substantially larger than the surface of the working electrode, leading to that the current generated is restricted by the working electrode. In the multivariate data analysis approach, only relative current values are correlated with each other. This means that the values of the absolute voltages applied to the working electrode with respect to a reference electrode are in principle not necessary to use for calculation. Thus, for these measurements the reference electrode can be omitted.

2.3. Data analysis

Data from voltammetric measurements in complex media are often difficult to interpret, especially if performed under non-equilibrium conditions. Multivariate methods, like principal component analysis (PCA) [12,13] and partial least squares (PLS) [12,13], have, however, shown to be useful. PCA is a mathematical tool, which utilizes the variance in experimental data. PCA decomposes the data matrix into latent variables called principal components. They are orthogonal to each other, and they successively define directions with as much variance as possible. A

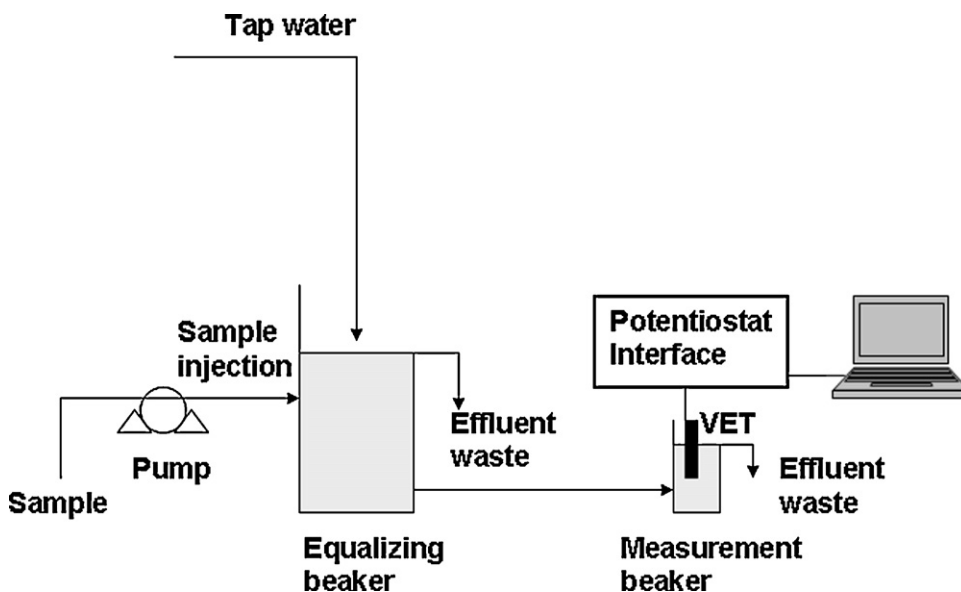


Fig. 3. Schematics of the experimental set-up. The voltammetric electronic tongue (VET) was placed in a measurement beaker that was separated from the equalizing beaker where the mixing of the tap water and the sample occurs.

score plot shows the relationships between the experiments, and groupings of them can be used for classification. PLS is used to make models from calibration sets of data. It is a linear method, in which PCA is performed on both the X-data (the voltammogram) and the Y-data (the different substances and their concentrations). Then a linear regression is performed on each principal component between the datasets and the Y-data, giving a regression model. This model can be used to predict values from the voltammograms. Since each measurement of the VET generates 288 datapoints, a large amount of data is generated. MVDA based on statistical methods, such as PCA and PLS, is, however, tolerant to this, and with a modern computer, calculations will only take few seconds. No pre-treatment of data was thus performed.

In PLS modelling, the prediction error is given by RMSEP (root mean square error of prediction), or, if corrected for bias, SEP (standard error of performance). One useful way of evaluating the prediction capacity of the model is to use the RPD (relative predicted deviation) value. This is defined as the standard deviation of the whole dataset divided by SEP, and for a useful model, this value should be 2 or above. The coefficient of determination, R^2 , also gives prediction error. It is defined as the sum of squared differences between actual and predicted values.

Principal component analysis and modelling using projection to the latent structure (PLS, also denoted partial least squares) were performed using the software SIRIUS 6.5 from Pattern Recognition Software, Norway.

2.4. Measurement system

Drinking water from the local water production plant was ran from a tap into a 1000 mL levelling beaker at a flow rate of 2100 mL min^{-1} . The distance from the tap to the levelling beaker was 500 mm, to ensure a broken water flow. The levelling beaker was connected to a 250 mL measurement beaker via a tube, with a flow rate of 2000 mL min^{-1} , and the surplus water was ran over the edge of the levelling beaker. A peristaltic pump was used to inject test compounds into the levelling beaker, and the electronic tongue was placed in the measurement beaker. By changing the pump speed, desired concentrations of compounds could be obtained in the measurement vessel. After changing the pump speed, it took around 5 measurement sequences for the new concentration to stabilize, equal to around five minutes. The peristaltic pump could be operated to deliver test compounds from 0.1 mL min^{-1} to 4 mL min^{-1} , giving a dilution rate of 1:20,000 to 1:500. The set-up is shown in Fig. 3.

The temperature of the drinking water was measured throughout the experiments, and only varied between 7.1°C and 7.6°C .

3. Results and discussion

3.1. Correlation studies of various compounds of interest for water quality

Initially the analytical ability of the system to separate various compounds of interest for water quality was investigated. The following compounds were chosen: NaCl (correlated to conductivity and sea water contamination), NaOCl (correlated to free chlorine, normally added to drinking water for disinfectant purposes), NaN_3 (a poison), NaHSO_3 (common product in waste water from power production plants), ascorbic acid (a reducing agent) and yeast (to simulate microbial contamination). NaN_3 was selected since this is a strong poison, ascorbic acid was selected only due to its pronounced redox properties. For NaOCl and NaHSO_3 , the concentrations were selected to normally levels in water production plants and power plants, respectively. The concentration levels

Table 1

Tested concentrations of various compounds for the correlation studies.

Compound	Conc. (mM)				
NaOCl (A)	0.1	0.2	0.3	0.4	0.6
NaN_3 (B)	0.05	0.1	0.2		
Ascorbic acid (C)	0.1	0.2	0.3		
NaCl (D)	0.6				
NaHSO_3 (E)	0.6				
Yeast (Y)	$0.1 \text{ (g L}^{-1}\text{)}$	0.2	0.3		

of NaOCl in water production plants are normally ranging from 0.2 mM and down. For NaCl, the concentration limit in drinking water is 3 mM and for NaHSO_3 it is 2 mM.

The choice of NaN_3 was made due to its physiological poisoning similarities of cyanide

The compounds were injected into the levelling beaker with varying pump speed to give different final concentrations in the measurement beaker, ranging between 0.05 and 1 mM for all compounds. For the yeast suspension, the concentration ranged between 0.1 and 0.3 g L^{-1} . When processing the data using MVDA, only values when the concentration had stabilized between different pump settings were used.

The concentrations of the tested compounds are given in Table 1.

A PCA plot for all compounds is shown in Fig. 4. They are all clearly separated, with a degree of explanation in the first principal component of 90%, in the second principal component of 5.4% and in the third 2.3%. Although it normally is difficult to give experimental meaning to the principal components, some interesting observations can be made from the plot. In principal, a VET can only obtain information concerning conductivity and redox activity. However, a large amount of hidden information in the signal patterns can be revealed by its combination with MVDA. This is due to that different metals have different catalytic properties, furthermore, also overpotential properties contribute with information. It has thus been shown, that a VET can be used for the prediction of pH, z-potential (the charge of a cellulose fibre) and chemical oxygen demand [14].

If an imaginary line is drawn from the zero point (where all concentrations equals zero) to the NaCl point (0.6D), this line should only represent the change in conductivity and not any contribution from redox properties. Lines drawn perpendicular to this line represent opposite redox properties (positive or negative potential) on each side of the line. Also other “hidden” properties may also contribute, such as e.g. overpotentials. Thus, e.g. NaOCl (A) has opposite redox potential (as being an oxidant) compared to e.g. NaHSO_3 (E)

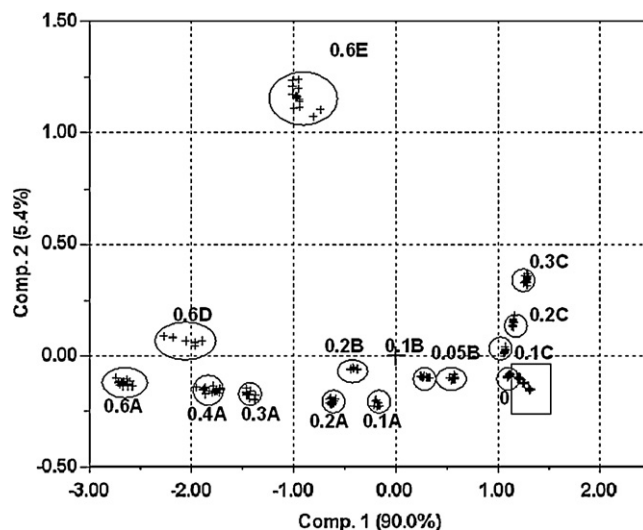


Fig. 4. A PCA plot of tested compounds of various concentrations, as given in Table 1.

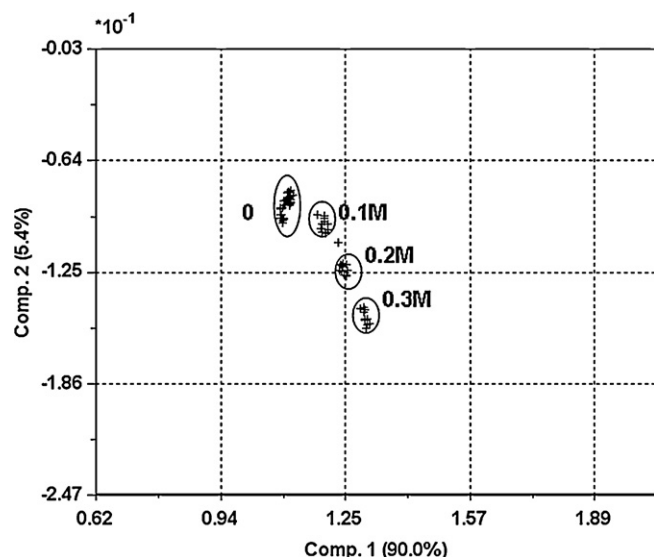


Fig. 5. An enlargement of Fig. 4 in the area close to origo, showing the yeast samples.

Table 2
Tested concentrations of various compounds for predictions.

Compound	Conc. (mM)					
NaOCl (A)	0.05	0.1	0.2	0.4	0.6	0.8
NaCl (B)	0.1	0.2	0.5			
NaHSO ₃ (C)	0.05	0.1	0.2	0.4	0.6	0.8

Table 3
Values of RMSEP, R^2 and RPD for crossvalidated predictions of the three compounds NaOCl, NaCl and NaHSO₃.

Compound	RMSEP	R^2	RPD
NaOCl	0.034 mM	0.961	7.0
NaCl	0.062 mM	0.955	3.9
NaHSO ₃	0.04 mM	0.975	6.0

and ascorbic acid (C) (as being a reducing compound).

The square marked area around zero concentration is zoomed to give Fig. 5, and it can then be seen that also the yeast samples separate. This shows that the information content of the voltammograms of tested compounds is very clearly separated and unique for each compound.

Since each cluster contains many measurements that are well collected, this implicates a very good reproducibility. This very good reproducibility is considered to be due to the self-polishing capability of the VET.

3.2. Multicomponent predictions

In a further estimation of the ability of the electronic tongue for multicomponent analysis of drinking water, the compounds NaCl, NaOCl and NaHSO₃ were chosen. As before, the compounds were injected at various concentrations in the measurement system, according to Table 2.

In Fig. 6, the resulting PCA plot is shown for each measured value, including the values for which the concentration had not yet stabilized. As can be seen, the compounds separate well.

Equilibrated data were also used for making a PLS based model for predictions. The model was used both for identification and prediction of concentration of the tested compounds. In Table 3, RMSEP values for cross-validated values for predicted versus true concentration for all three compounds are shown, as well as values for R^2 and RPD, and as can be seen, with very good results.

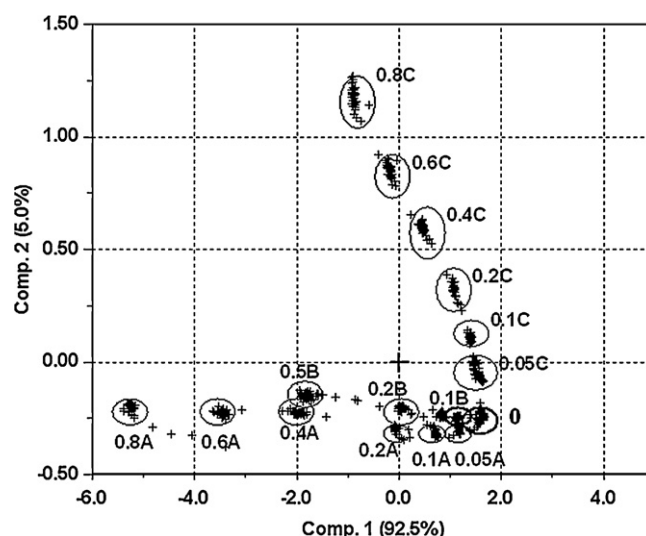


Fig. 6. A PCA plot of tested compounds of various concentrations, as given in Table 2.

RMSEP values for crossvalidated predictions of the three compounds were for NaOCl 0.034 mM, for NaCl 0.062 mM and for NaHSO₃ 0.04 mM, indicating an excellent correlation.

4. Conclusions

In this article, the potential of using a voltammetric electronic tongue for multicomponent analysis of compounds in drinking water has been demonstrated. In this investigation, only pure solutions were investigated to show the properties of the VET. In future studies, also mixtures of contaminants will be studied.

By utilizing this type of non-selective sensor, it is possible to detect a plurality of anomalies without the need of a specific sensor for each type of event. This property combined with the robustness of the voltammetric electronic tongue and the possibility to operate it without the use of a common reference electrode makes it a powerful tool for drinking water surveillance.

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