Thesis

Method to decrease the disturbing effects occurring by the electronic tongue measurement

Prepared by

Zoltán Kovács

Supervisor:

András Fekete, DSc

Corvinus University of Budapest

Faculty of Food Science

Department of Physics and Control

Budapest, 2012

PhD School

Name: PhD School of Food Science

Field: Food Science

Head: Péter Fodor, DSc
Corvinus University of Budapest

Supervisor: András Fekete, DSc
Department of Physics and Control
Faculty of Food Science
Corvinus University of Budapest

The applicant met the requirement of the PhD regulations of the Corvinus University of Budapest and the thesis is accepted for the defence process.

.... Signature of Head of School

.... Signature of Supervisor

Introduction

Generally the human taste sensing cannot be replaced by instruments. However, the sensory evaluation has many drawbacks like the subjectivity and fatigue of the panel members and there are tasks where the human sensory evaluation is impossible. Therefore, there is an increasing need for an instrument which can measure the quality or some quality parameters of the samples in an objective way. The electronic tongue and taste sensors were developed to satisfy these requirements. The principle of the concept is to measure with sensors having cross-sensitivity and partial selective character similar to the human tongue. Therefore, the sensors are able to measure the complex substances solved in the liquids. The result that we can obtain with such an instrument is a chemical pattern characteristic for the definite sample. This is the so called “fingerprint” technology.

In the literature there are publications dealing with instrumental taste sensing from the nineties. The number of the articles related to this topic increased continuously in the last two decades. However, in spite of the wide range of the application examples there are only few publications that show the results of the comparison of measurements performed in different times. However, the sensor drift is a difficult problem. According to some scientists the electronic tongue can be a useful instrument for monitoring as well, but for this purpose it is necessary to solve the problem of the drift (Krantz-Rülcker et al. 2001). It is necessary to get know more in this field that can be done only by empirical methods (Vlasov et al. 2002).

The drift could occur because of temperature changing, not satisfactory cleaning and because of the so called memory effect. These phenomena could be observed in case of the different sensors. Escuder-Gilbert and Peris (2010) wrote that the drift can be decreased by controlling the temperature and using appropriate cleaning method. According to Ivarsson et al. (2001) there are two way to decrease the drift: using mathematical correction or improving the measurement system. The drawback of their drift correction method is that the tendency of the drift must be in the reference sample similar to that of the tested samples.

The problem of stability is an important issue of the ISFET based electronic tongue. Such an instrument has high sensitivity, but there are several disturbances (Oelssner et al. 2005). There are publications related to the electronic tongue dealt with the drift, but it is not analyzed in detail.

Therefore, it is necessary to develop new drift correction methods for application.

OBJECTIVES

The objectives of the work reported were to, as follows:

- Determination of the influence of the disturbing effects on the sensor signals during the measurement with Alpha Astree electronic tongue. Therefore, tasks were as follows:
  - determination of the effect of temperature on the sensor signals and to develop mathematical model for the correction of the temperature effect,
  - determination of the memory effect on the sensor signals and to develop method to minimize this effect,
  - determination of the effect of cross contamination on the sensor signals and the development of method to minmize this effect.
- Development of a drift correction method to be able to compare the results of electronic tongue tests measured in different times, by chemical and mathematical methods.

MATERIALS AND METHODS

An Alpha Astree type electronic tongue was used for my experiments. This instrument contains a sensor array including seven Ion Sensitive Field Effect Transistor based potentiometric chemical sensors for food applications and an Ag/AgCl reference electrode (Metrohm). The chemical sensor has different organic membrane coatings. Due to the coating type, the sensors are cross-selective and cross-sensitive to different taste attributes. The so called fingerprint can be observed with this method.

Effect of temperature on the sensor signals

Experiments were performed with different model solutions at different temperatures. The tested samples were different model solution and apple juice samples at 5, 15, 25, 35°C.

In a sequence I analyzed only one type of model solution (0.01M citric acid or glucose or NaCl or caffeine or MSG solution).

The apple juice samples were made from commercial apple juice diluted with distilled water. I tested 80, 85 90, 95 and 100% apple juice samples at the mentioned temperatures.

Effect of cross contamination

Commercial apple juice in 100% concentration was used for the determination of the effect of the cross contamination. During the electronic tongue measurement the pH and the conductivity of the apple juice samples and the cleaning solutions were measured before the 1st, 3rd, 5th, 7th and 9th repeat.

Analysis of the memory effect

I analyzed the memory effect with the measurement of different model solutions and liquid foods.

Apple juice in 100% concentration and 0.01M model solutions (citric acid, NaCl and MSG solution) were tested in three different measurement sequences.

Different concentrations of coffee drinks were also analyzed. The coffees were measured with 3,6g/100ml, 0,36g/100ml, 0,036g/100ml concentration using three parallel samples from each ones.

Determination of the optimal measurement concentration

Different commercial soy drinks were evaluated in different concentrations (25, 10 and 1%). Five different brands were tested in the same concentration in each measurement.

Comparison of the different drift correction methods

I developed a drift correction method for the Astree electronic tongue. I tested this method with the measurements of apple juice samples.

The drift correction method of Alpha Astree manual the so called „component correction" introduced by Holmin et al. (2001) and my drift correction method were compared with the measurements performed on apple juice samples and model solutions (such as 0.01M citric acid, NaCl, MSG solution). The same tests were performed on five different measurement days.

During the first four tests the cleaning solutions applied in the electronic tongue sequence were exchanged after every cleaning to avoid the effect of cross contamination and memory effect.

In the fifth test the cleaning solutions were not replaced.

The tests were performed under controlled (25°C) temperature.

Applied statistical methods and softwares

Different statistical methods were applied for the statistical evaluation.

Principle component analysis was used for the evaluation of the effect of temperature on the sensor signals. Furthermore, I evaluated the residuums and performed Durbin-Watson statistics. The results of apple juice measurement were evaluated by discriminant analysis too.

One- and two-way analysis of variance was used for the evaluation of the effect of cross contamination and memory effect. Tukey tests were performed where it was necessary.

For the evaluation of the memory effect principle component analysis was also used. Furthermore, I calculated the Euclidian distance between the sample groups.

MathCad ver. 14.0 mathematical software was used to my drift correction method. I developed a program, which was able to calculate the transformed data matrix based on the raw data.

To compare the different drift correction methods discriminant analysis was used and the Mahalanobis distances of the sample groups were also calculated and evaluated.

RESULTS AND DISCUSSION

Effect of temperature on the sensor signals

Figure 1. shows the principle component analysis result of the **citric acid** measurement. The groups of the samples having different temperature are separated based on the first principle component in the right order. This result demonstrates that the temperature had a significant effect on the sensor signals. The results of the detailed data evaluation showed that the relationship between the sensor signal and the sample temperature can be approximated by linear connection except for two sensors. The linear transformation gave satisfactory result for the correction of the temperature effect.

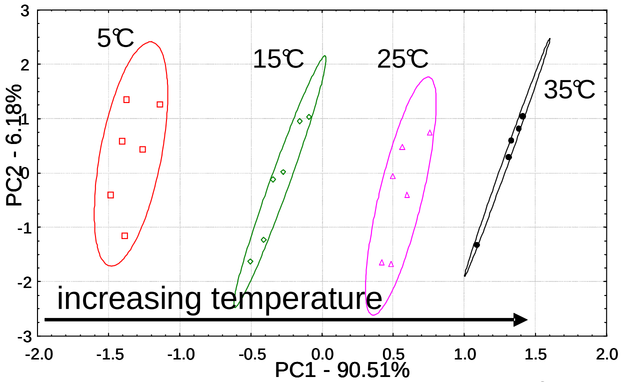


Figure 1. Principle component analysis of citric acid solutions (PC1-PC2)

The relationship between the sensor signal and the sample temperature was approximated by linear connection except for three sensors in case of **glucose, NaCl solution** and **apple juice samples**. The linear transformation gave a satisfactory result for the correction of the temperature effect.

The result of the principle component analysis plot of the **caffeine** measurement results (Figure 2.) determined the sample groups having different temperatures showed separation according to PC2 as well. The results of the detailed data evaluation showed that the relationship can not be approximated by linear connection. The correction of the temperature effect can be performed only with non-linear transformation.

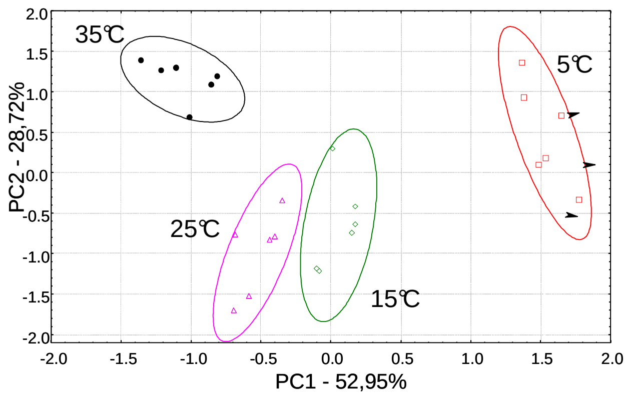


Figure 2. Principle component analysis of caffein solutions (PC1-PC2)

The results of the measurements performed with **MSG solutions** showed similarities to the results of the caffeine test. Thus the relationship can not be approximated by linear connection. The correction of the temperature effect can be performed only with non-linear transformation.

The results of the measurements performed with the apple juice samples of different concentration and temperature values were evaluated with discriminant analysis. Figure 3. shows the results. The apple juice samples having different temperatures were discriminated based on the first factor (Root1), which contains about 98% of the variance between the groups. The apple juice samples of different concentrations were discriminated based on the second factor (Root2), which contains only 2% of the variance between the groups.

The Euclidian multidimensional distances were calculated between a reference group and the other groups. In case of the examination of the temperature effect the group of the 5°C sample, while in case of the examination of the concentration effect the 80% sample was the reference (Figure 4.).

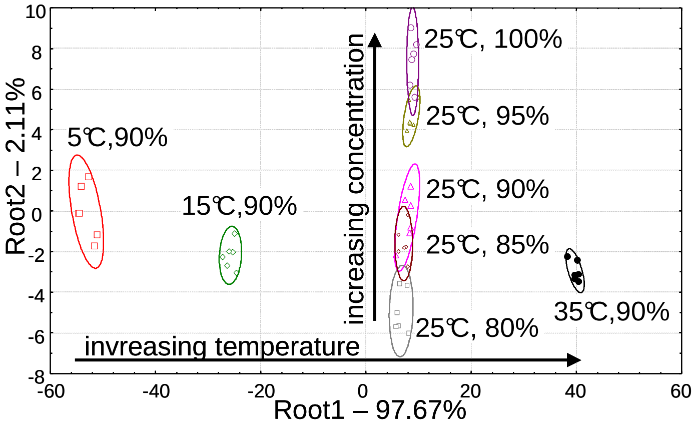
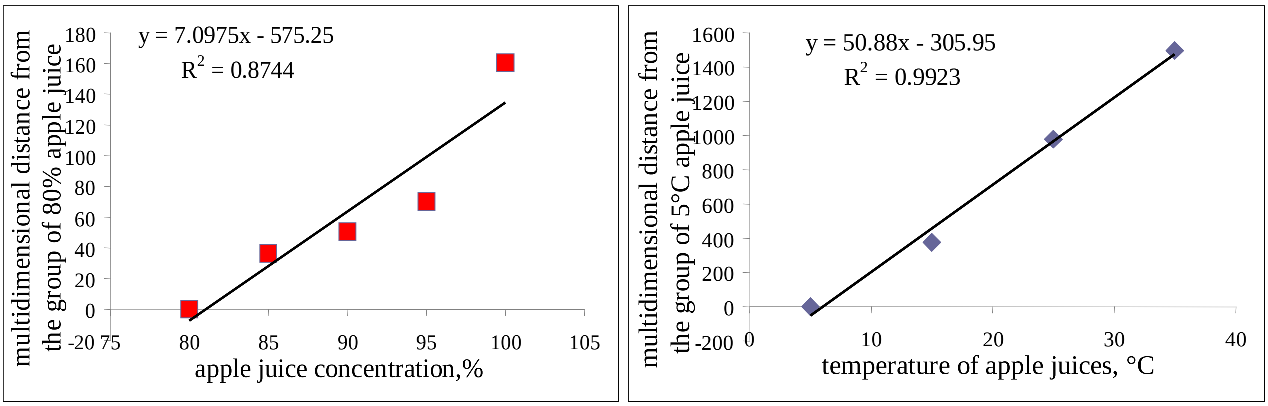


Figure 3. Discriminant analysis of apple juice samples

1°C temperature difference was caused about 50 intensity differences. 1% concentration difference caused about 50 intensity differences in the Euclidian multidimensional distance.



a, b,

Figure 4. Euclidian multidimensional distance between the groups of apple juices: (a) with different concentrations, (b) with different temperatures

Effect of cross contamination

To describe the effect of the cross contamination the pH and the conductivity of the apple juice samples and the cleaning solutions were measured during the electronic tongue measurement. Figure 5. shows the results of the pH of apple juice samples as the function of the measurement repeats. The pH of the apple juice increases approximately by 0.1 pH in a repeat because of the distilled water transmitted

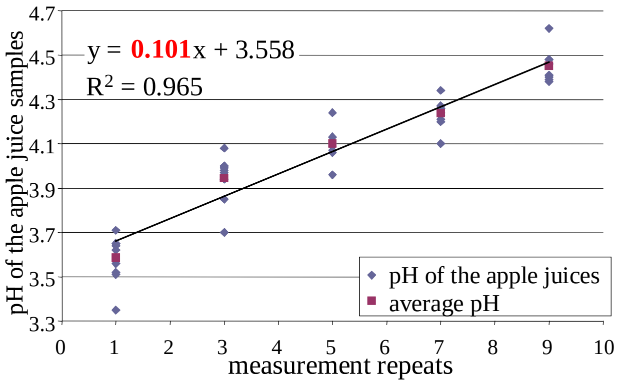
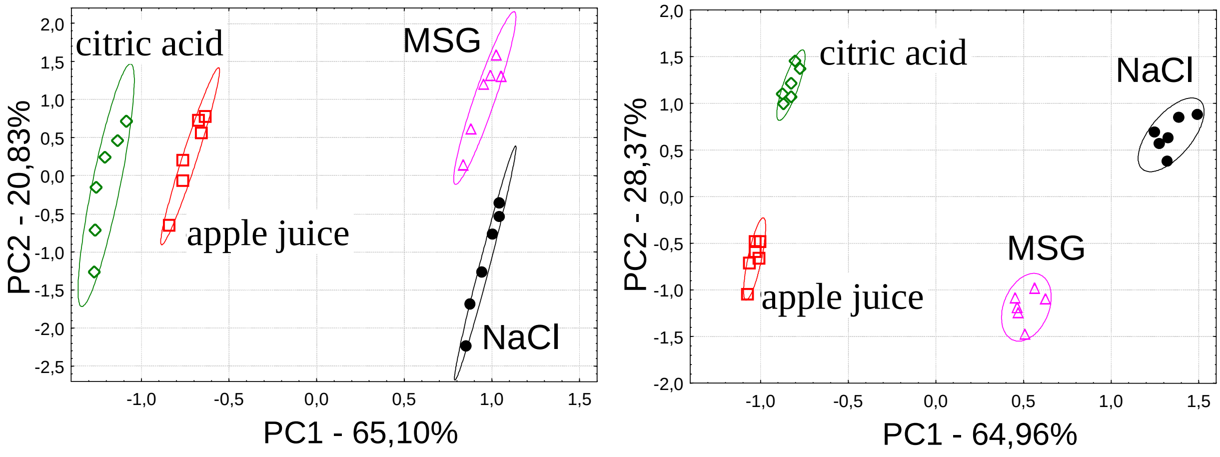


Figure 5. The increase of pH of apple juice samples versus measurement repeats

by the sensor head. Therefore, I observed that the solution transferred by the sensor head modified the pH and the conductometry of the apple juice samples and the cleaning solutions. This phenomenon confirmed that the cross contamination can cause problem during the electronic tongue measurement.

Analysis of the memory effect

Figure 6. shows the results of principle component analysis evaluated on the apple juices and model solutions measured in different sample order. The sample order was: either „citric acid →NaCl →MSG →apple juice” (a), or „apple juice →MSG →NaCl→ citric acid” (b). The relative position of the sample groups according to the principle component plot was different from each other.



(a) (b)

Figure 6. Principle component analysis plot of apple juices and model solutions measured in different sample order

The results of the detailed data evaluation showed that the measurement of the apple juice samples and model solutions applying different sample order resulted significant differences on the Euclidian distances between the sample groups, it is because of the memory effect.

Figure 7. shows the principle component analysis results of the different coffee sample concentrations: 3.6g/100ml, 0.036g/100ml, and 0.36g/100ml. Based on PC1 the samples had different concentrations. The parallel coffee samples in 3.6g/100ml and 0.036g/100ml concentrations show separation based on PC2, which contains

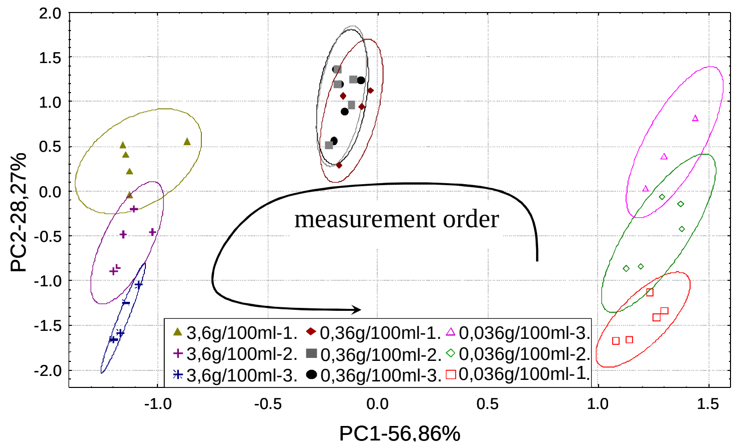


Figure 7. Princple component analysis plot of the different coffee sample concentrations

28% of the total variance, while the parallel samples of the 0.36g/100ml concentration are overlapping. The separation based on PC2 is equal to the measurement order. This phenomenon confirmed the memory effect.

Determination of the optimal measurement concentration

Figure 8. shows the relative standard deviation of the sensor signals observed during the measurement of the three soy juice samples of different concentrations. The lowest deviation was found in case of the 1% concentration sample with all the sensors (expect sensor GA).

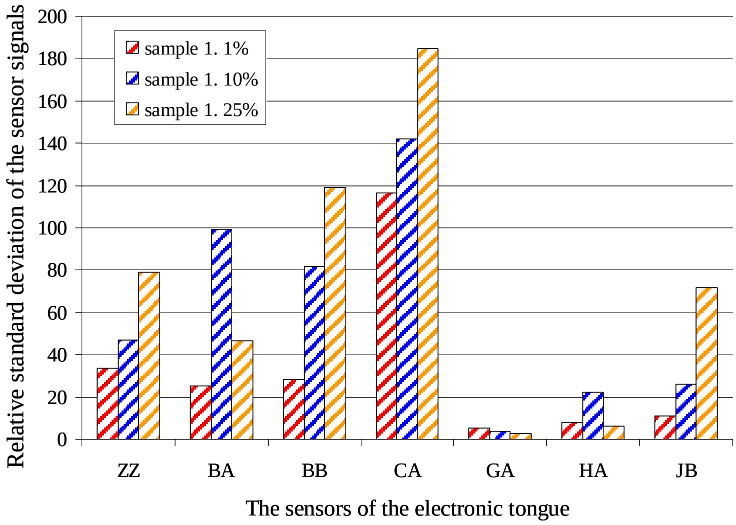


Figure 8. Relative standard deviation of the sensor signals observed during the measurement of the different soy juice sample concentrations

In case of the coffee and soy juice samples the standard deviation of the measurement results depended on the concentration of the samples. Therefore, a definite concentration range was determined to get a lower standard deviation.

Comparison of the different drift correction methods

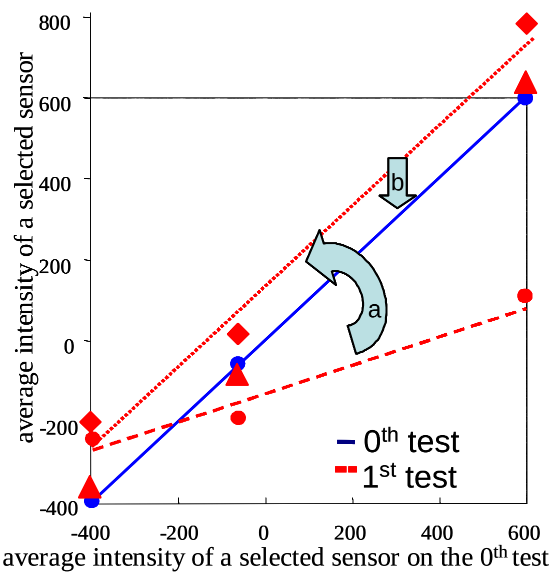


Figure 9. Scheme of the mathematical drift correction method

Drift correction method is necessary to compare the results of electronic tongue tests performed in different times. I developed a drift correction method. According to this method the measurement of the model samples together with the analyzed samples are also needed.

After that a mathematical correction method is performed:

1st step: outlier detection of the measurement results of the first test (0th test).

2nd step: the average of the sample groups are calculated based on the individual sensors. After that the averages are plotted in a way that y = x (blue dots and blue line). The samples measured later will be transformed to this blue line.

3rd step: the average of the reference sample groups of the next measurement (1st test) are calculated based on the individual sensors. These sample groups are plotted as the function of the sample groups of the 0th test (red dots).

4th step: fitting a line to these points using the partial least square method and determination of the parameters of this line (red dashed line).

5th step: transformation of this red dashed line to the blue line in 2 steps. First the transformation of the intercept is performed („a" arrow) this results the red diamonds and red line, than a linear shift is applied („b" arrow) resulting the red triangles.

These steps must be performed with all the sensors.

Three different drift correction methods were compared on the results of apple juice measurement:

- **AlphaSoft** developed by AlphaMOS,
- the method introduced by **Holmin et al.** (2001) and
- my drift correction method (**own method**).

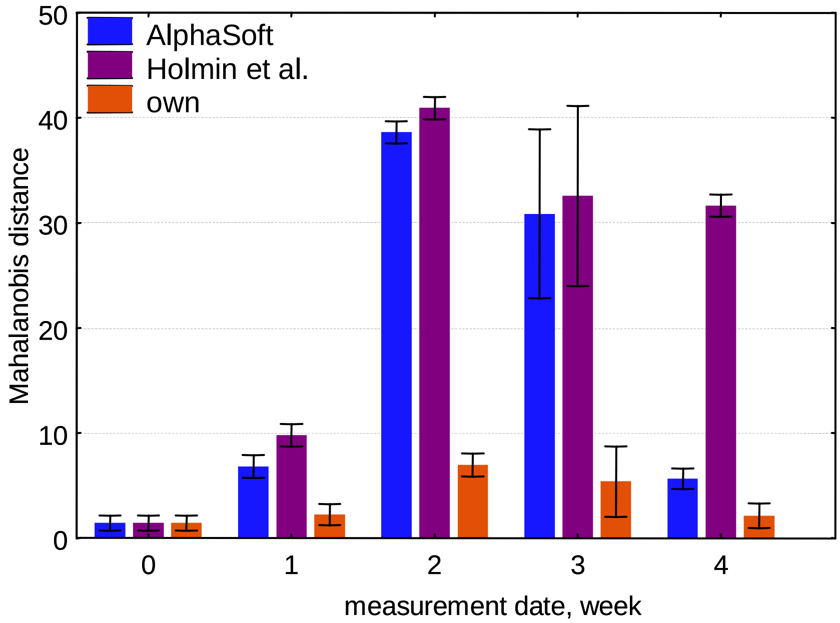


Figure 10. Mahalanobis distances determined by the different drift correction methods with apple juice samples

The Mahalanobis distances calculated between the group center of apple juice measured during the first measurement and the measurement points of the further measurements were the shortest using my drift correction method. Therefore, my method is suitable for sensor drift correction.

NEW SCIENTIFIC FINDINGS

Based on the experiments performed with the Alpha Astree electronic tongue – using the sensors specified by the producer as ZZ, BA, BB, CA, GA, HA and JB (array #1) – the following new scientific findings were determined:

Temperature dependence

1. It was observed that the effect of the measurement temperature on the sensor signal depends on the different sensors and the measured samples when measuring 0.01M citric acid, glucose, NaCl, caffeine and MSG model solutions and 90% apple juice samples.
2. The results showed that the sensor signals observed at 5, 15 and 35°C can be transformed to the results observed at 25°C:
   - with linear transformation in case of 0.01M citric acid, NaCl and glucose MSG model solutions and 90% apple juice samples, and
   - with non- linear transformation in case of 0.01M caffeine and MSG model solutions.
3. The results showed that the differences in the sensor signals is bigger when measuring apple juice samples of a definite concentration but with 30°C temperature differences than with apple juice samples of a definite temperature but with 20% concentration differences. The Euclidian multidimensional distances were calculated between the groups of apple juice samples having temperature between 5-35°C and concentration between 80-100%. It was observed that the change of the temperature with 1°C resulted approximately seven times bigger effect on the sensor signal than 1% concentration change.

Cross contamination

4. The results of different apple juice sample measurements showed that the solution transformed by the sensor head modified the pH and the conductivity of the juices and the cleaning solutions. This confirmed the effect of cross contamination. The pH of the apple juice samples was increased by approximately 0.1 pH in the repeats because of the solution quantity transmitted by the sensor head. The conductivity of the cleaning solution with apple juice samples increased by approximately 0.04 $mScm^{-1}$ in the repeats because of the solution transmitted by the sensor head.

Memory effect

5. The measurement results of NaCl solutions having different concentrations showed that the classification power of the linear discriminant analysis is worst if the measurement is performed with random sample order instead of the systematic one. The total classification power was 91% when testing NaCl solutions of different concentrations (such as 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and

10^{-6} M) and distilled water according to the systematic sample order However, approximately 80% was the classification power with the random sample order

6. The results of the measurements performed with 100% apple juice samples and 0.01M citric acid, NaCl and MSG model solutions when applying different sample orders resulted in significant differences according to the Euclidian distances between the sample groups. This shows the influence of the memory effect. These results are conformed by the principle component plot of the tested model and apple juice samples.
7. The measurement results of 0.036g/100ml, 0.36g/100ml and 3.6g/100ml concentration coffee samples showed the memory effect, as well. The principle component plot of the parallel samples of the 3.6g/100ml and 0.036g/100ml concentration coffee sample results showed separation according to the measurement order based in PC2 which contained 28% of the total variance.

Optimal concentration for measurements

8. The standard deviation of the measurement results of coffee and soy bean juice samples depended on the concentration. Therefore, a definite concentration range can be determined to get a lower standard deviation. The lowest standard deviation was found with the soy bean juice samples the at 1% concentration, while with the coffee samples at 0.36g/100ml concentration within the tested range.

Drift correction

9. I developed a drift correction method to compare the results of electronic tongue tests measured in different times. According to this method the measurement of at least two model samples are also needed together with the analyzed samples. After that a mathematical correction method is performed, as follows:
   - The average of the measurement results of the model samples were calculated for the first and the second tests. After that the averages of the second test are plotted as the function of the average of the first test.
   - A line was fitted to these points by the means of partial least squares method.
   - This line was transformed to the y = x line. At first the intercept was set by rotation and then the slope by linear shifting.
   - This transformation was applied to the results of the samples, as well.

   The method was tested with apple juice samples and model solutions. The results showed that the method was suitable for minimizing the disturbing effect. The Mahalanobis distances were calculated between the group center of apple juice measured during the first measurement and the measurement points of the further measurements. The shortest distance was obtained by my drift correction method.

RECOMMENDATION FOR FURTHER RESEARCH

The recommendations are as follows:

- Further evaluations are necessary concerning the effect of the temperature on the sensor signals to be able to compare the results of tests performed at different temperatures. These experiences could provide possibility for the comparison of tests performed under laboratory and factory conditions.
- The determination of the optimal measurement temperature for the different type of samples. It provides with smaller deviation during the measurement.
- Experiments are proposed with the application of lubricants to decrees the effect of cross contamination.
- Different type of cleaning solutions should be determined for the different sample types to decrease the memory effect.
- The determination of the optimal measurement concentration for the different type of samples to decrease the deviation of the results of electronic tongue tests.
- The development of reference solutions specifically for different sample groups to decrease the memory effect.
- The determination of reference solutions for the different sample types to be able to apply my drift correction method. These solutions have to fit to the type of the samples.
- The application of my drift correction method and the development of a database to support it.

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ACKNOEWLEDGEMENTS

I would like to express my thanks

- to my supervisor **Dr. András Fekete,**
- to **Dr. Viktória Zsom-Muha,**
- to **Dr. József Felföldi,**
- to **Dr. István Dalmadi**
- to **Dr. János Zana** and
- to all my colleagues at the Department of Physics and Control
  Faculty of Food Science, Corvinus University of Budapest

I would like to also thank:

- to **Dániel Szöllősi**
- to **Evelin Várvölgyi** and
- to **my further colleges and students**.

I would like to thank for the possibility of cooperation

- to **Dr. Virág Sági-Kiss,**
- to **Dr. Károly Héberger,**
- to **Dr. László Sipos** and
- to **Dr. Zoltán Kókai.**

I would like to express my special thanks to Mrs. Dr. János Karai for supporting my work with the Karai Predoctoral Scholarship.

I express my deepest thanks to my wife and my family for the support my work during the PhD period.

Thanks for TÁMOP 4.2.1/B-09/1/KMR/-2010-0005 and 4.2.2/B-10/1-2010-0023.