



## Multivariate calibration transfer between two different types of multisensor systems



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### ABSTRACT

The most popular sensors in multisensor systems (electronic tongues) are voltammetric and potentiometric ones. Practical application of multisensor systems for evaluation of particular target parameters requires calibration step. Even if both types of sensors (voltammetric and potentiometric) can be sensitive towards the same parameter of an analyte and can be used for its quantification, corresponding multisensor systems cannot operate in the framework of a single unified calibration model interpreting the responses of both systems. This research is dedicated to experimental verification of calibration transfer feasibility between voltammetric and potentiometric multisensor systems. The algorithm of direct standardization suggested earlier in spectroscopy was applied for transformation of potentiometric data into voltammetric format, and vice versa. Such transformations allowed for interpretation of a system response by multivariate regression model built employing the data from another type of multisensor system. For example, concentration of the tartaric acid in the grape musts can be determined with the regression model developed for voltammetric system using the data obtained from potentiometric system. Only 20% decrease in precision was observed for the converted potentiometric data compared to initial voltammetric model.

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### 1. Introduction

Traditionally taste and flavor of the food products are being evaluated by trained sensory panel. Implementation of analysis by humans makes taste assessment quite subjective and depending on mood or health conditions of a particular panelist, even well-trained. Besides, these types of tests are time-consuming, since samples usually cannot be analyzed on-site and have to be collected and transferred to special laboratory. Therefore, development of an apparatus, which could be capable of taste assessment in terms of human taste panel, is strongly demanded. Artificial sensory systems were suggested as analytical tools suitable for this type of measurements in food and pharmaceutical industries. Such devices are intended to simulate human sensory organs performance, such as tongue, and they can assist human sensory panels in routine taste

assessment. Multisensor systems, also widely known as “electronic tongues” consist of an array of cross-sensitive chemical sensors and appropriate data processing engine [1]. Significant advantages of artificial sensory system are operation simplicity and fast availability of the results. It was shown that multisensor systems can be employed to solve different problems, like e.g. counterfeit recognition [2], taste evaluation [3–5], chemical composition analysis [6–8], etc. Another interesting feature of such artificial systems is that obtained results can be expressed, if needed, in various scales, such as concentrations [9], particular taste attribute intensity [10] and other integral characteristics [11,12].

Different types of multisensor systems for liquid analysis can be distinguished depending on the mode of analytical signal generation: voltammetry, potentiometry, impedance, etc. [13] Sensor responses are usually interpreted with the help of different machine learning techniques, commonly known as chemometric techniques in chemical context. Calibration is a necessary step of application of multisensor systems, just as of any other analytical method, for numerical prediction of certain properties or attributes. Calibration is intended to relate the response of the sensor system to target parameter in a framework of a dedicated mathematical

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model. Reliability and accuracy of results obtained with multisensor systems are strongly correlated with calibration model quality and the development of an appropriate model is a crucial step. Establishment of a robust calibration model requires representative sample set and samples have to be studied by traditional analytical method(s) in order to get reference values for model training and validating. An example of a typical calibration procedure for a multisensor system can be found e.g. in [14]. This research dealt with taste and quality assessment of wines. Calibration routine assumed freezing/thawing of samples, their storage at controlled temperature, dilution and analysis with numerous reference methods for 63 different wine samples. The overall protocol was time and resource consuming.

Once the mathematical calibration model is established it could only be used for a limited period of time and with this particular sensor array. An application of the model built for potentiometric sensor array for prediction of voltammetric sensor array performance is currently not possible due to obvious mathematical restrictions. However, such an opportunity would be highly attractive, because the majority of electronic tongue research was made using two electrochemical methods: voltammetry or potentiometry [15]. There are certain mathematical approaches suggested mainly in NIR spectroscopy for the so called calibration transfer between two devices that may have different sensitivity and shifted wavelengths in spectra and, thus, cannot employ the same regression model [16–18]. These methods are based on correction (standardization) of response of one of the instruments in order to make its response suitable for use with regression model for another one. One of the most popular algorithms for calibration transfer is piecewise direct standardization (PDS) [19]. This method was successfully applied for various spectrometric [18,20], voltammetric [21–24] and potentiometric [25,26] data. The application of the PDS assumes that two datasets from two instruments have the same size and nature, thus it cannot be applied for standardization of two different sensor arrays. A predecessor of PDS – direct standardization method (DS) – was also intended for transfer of the models between two similar instruments [16], however its mathematical structure allows for handling the data of different dimensionality. Thus, in principle, it is suitable for calibration transfer between two different sensor arrays.

This study is dedicated to evaluation of the calibration transfer feasibility between different types of multisensor systems producing different analytical signals: voltammetric and potentiometric. As a case study we addressed the task of quality parameters prediction in grape wine musts. These musts have rather complex chemical composition and, thus, represent quite typical sample's type for electronic tongue experiments.

## 2. Materials and methods

### 2.1. Samples

8 types of grape musts were analyzed. They were produced by crushing up fresh red grapes of eight varieties (Tempranillo, Garnacha, Cabernet, Prieto Picudo, Juan García, Rufete, Mencía Regadío and Mencía Secano) harvested in 2014 in the Castilla y León region (Spain) by the Enological Centre of Castilla y León (Agrotechnology Institute of the regional Government – ITACYL), and by a cellar association of the region (Bodega Cooperativa de Cigales). To obtain the musts, 200 berries of each variety were introduced in a plastic bag and crushed for one minute. The musts were separated from the seeds and peels by decantation and analyzed. Musts thus obtained were dispensed in 50 ml glass tubes and frozen at  $-20^{\circ}\text{C}$ . Before analysis, samples were unfrozen at  $4^{\circ}\text{C}$  during 24 h.

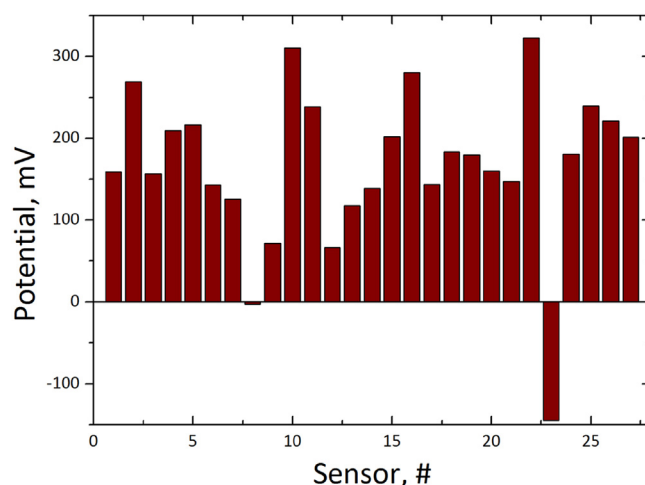


Fig. 1. Raw responses of the potentiometric multisensor system in Cabernet Sauvignon must.

### 2.2. Sensor systems

#### 2.2.1. Potentiometric multisensor system

Potentiometric sensor array consisted of 26 cross-sensitive sensors. 10 sensors were anion-sensitive poly(vinyl chloride) plasticized membranes, 11 sensors were cation-sensitive. These sensors were based on various lipophilic organic ion-exchangers and ligands. Details on typical sensor compositions are available elsewhere [27]. The rest of the sensors were standard glass pH electrode, platinum RedOx sensor and four chalcogenide glass electrodes with pronounced RedOx sensitivity. Potentiometric measurements were carried out using the following procedure. Sensors were conditioned in a must of Mencía Secano for 1 h before each experimental day. After that the array was rinsed with several portions of distilled water and dried with filter paper. Sensors were immersed into sample solution and potentials were registered every 8 s during 3 min, then the three last readings were averaged for further processing. Each sample was measured at least in three replicas that were also averaged for data analysis. All the measurement results formed matrix  $X_p$  (8 samples  $\times$  27 sensors). Typical response of potentiometric multisensor system in one of the samples is shown in Fig. 1.

#### 2.2.2. Voltammetric multisensor system

An array formed by four CPE electrodes was prepared as previously reported by mixing graphite powder and the corresponding metal oxide nanoparticle (15% w/w) [28]. Nujol was used as binder of the composite mixture and a metallic copper wire was used as contact. Pastes were packed into the body of a 1 ml plastic syringe and compressed. The array was formed by three electrodes modified with metal oxides nanoparticles including  $\text{TiO}_2$  ( $\text{TiO}_2\text{NP-CPE}$ ),  $\text{CeO}_2$  ( $\text{CeO}_2\text{NP-CPE}$ ),  $\text{NiO}$  ( $\text{NiONP-CPE}$ ) and one unmodified carbon paste electrode (C-CPE). The electrochemical measurements were carried out in a standard three-electrode cell using  $\text{Ag}/\text{AgCl}/\text{KCl}$   $3\text{ mol l}^{-1}$  as reference electrode, a platinum plate as counter electrode and the CPE electrodes as working electrode. The potentiostat was an EG&G PARSTAT 2273 potentiostat/galvanostat.

Cyclic voltammograms were registered 7 times in each type of the must in a voltage window from  $-0.8$  to  $1.0\text{ V}$ . Typical response of voltammetric sensors is presented in Fig. 2(a). Data processing can be performed with the whole voltammograms, but it was shown that a pre-treatment step with Kernel methods in such systems makes information extraction more efficient [29]. According to this algorithm voltammetric response curves were divided into the regions by bell-shaped windowing function and these windows

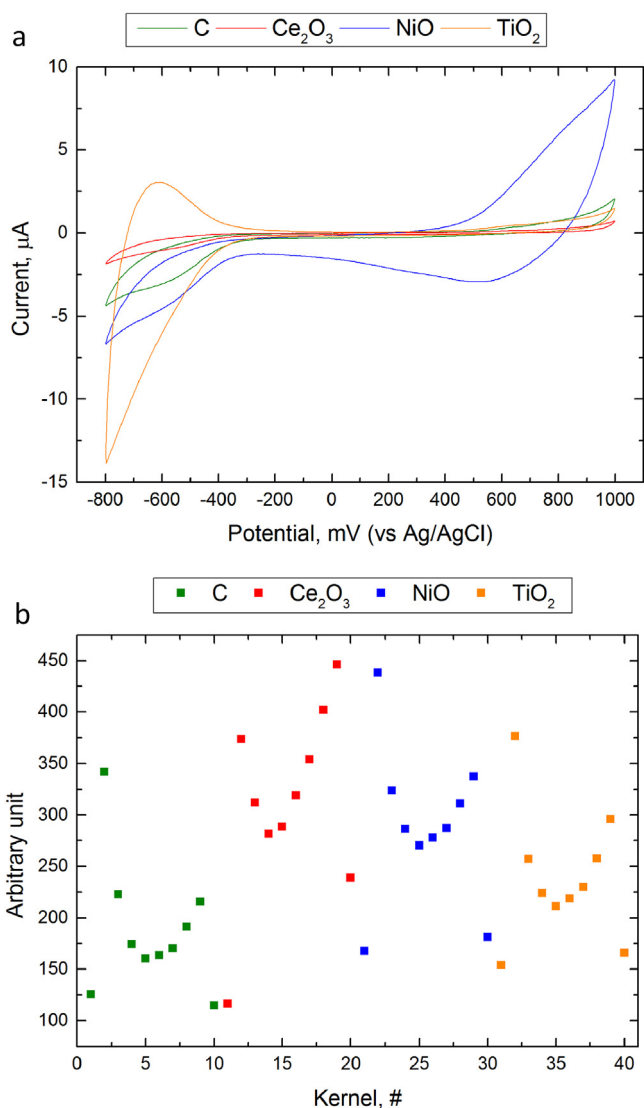


Fig. 2. Raw responses of the voltammetric multisensor system in Cabernet Sauvignon must (a) and kernels calculated from the voltammograms (b).

were integrated with respect to potential. As a result, each voltammogram was represented by 10 kernels (Fig. 2(b)). These kernels were combined into matrix  $X_v$  (8 samples  $\times$  40 kernels (for all 4 sensors)) which was further used for data processing.

### 2.3. Reference methods

The following parameters in the musts were evaluated by traditional analytical techniques: total acidity, concentration of tartaric and malic acids, pH, concentration of potassium, sugar content, sugar content in terms of Brix degrees and total phenol content index (TPI). The chemical analysis was carried out by Enological Centre of Castilla y León using standard International methods as described by the OIV [30]. Obtained values were used as reference data for regression modelling of both multisensor system responses.

### 2.4. Measurements

Musts were unfrozen in the fridge at +4 °C during 24 h before measurement. Then 30 ml aliquot of the must was taken and diluted with deionized water. Both voltammetry and potentiometry are

electrochemical methods; however, there are certain differences in a way of analytical signal formation and, as consequence, in optimal measurement conditions. Higher must content in the analyzed sample leads to better reproducibility, but increases the washing time. According to the preliminary study dilution ratio for potentiometric measurements was set to 3:7 (must:water), this proportion provides for optimal balance between intensity of analytical signal, reproducibility of the signal and duration of sensor washing procedure. Analysis with voltammetric sensors was done in 25 ml of must with dilution 1:1. To reduce possible systematic errors all replicated measurements in the samples were performed in a random order.

### 2.5. Data processing

In order to visualize data structure Principal Component Analysis (PCA) was used. PCA is an unsupervised projection method and it allows for reducing the dimensionality of the data with minimal loss of the information [31].

Partial-least squares (PLS1) regression 1 was employed to build the quantitative prediction models [32]. The results of potentiometric measurements  $X_p$  and preprocessed data from voltammetric sensors  $X_v$  were taken as predictors. Reference data on various chemical parameters were used as dependent variables. PLS is a linear method and it supposed that there is a linear dependency between predictors and dependent variables. Potentiometric sensor responses are linear against logarithm of concentration according to Nikolsky-Eisenman formalism. In case of voltammetric sensors there are typically no special restrictions regarding the scale of dependent variables. In principle, original voltammetric PLS models produced against non-logarithmic concentrations may have better metrics, however, in order to be able to perform calibration transfer, both systems should be calibrated in the same scale and logarithm of concentration was chosen for further studies. Thus 16 PLS models were obtained, 8 of them relating the response of voltammetric multisensor system with target parameters and 8 for the response of potentiometric sensor array. The PLS models were validated by full cross validation and the root mean square errors of cross validation (RMSECV) were calculated. PCA and PLS processing was done with the Unscrambler 9.7 software (CAMO, Norway), while the rest of the chemometric processing was done by specific routines in MatLab R2015b (MathWorks, Natick, MA).

It is obvious, that PLS models obtained with voltammetric data are not suitable for interpretation of the potentiometric data, and vice versa. The reason for this is the different number of predictive variables and different data structure in the two multisensor systems.

The mathematical procedure – direct standardization – can be employed to circumvent this. Initially this method was suggested in spectroscopy as an alternative to recalibration [16]. DS procedure relates the responses of two instruments in the same samples through calculation of correction matrix of coefficients. Application of matrix pseudoinverse operation provides for an opportunity to avoid problems with different number of independent variables in the response of two instruments. The following procedure of the data transformation was employed: transfer (standardization) subsets  $X_{vff}$  and  $X_{pff}$  were chosen from matrices  $X_v$  and  $X_p$  using the algorithm proposed by Kennard and Stone [33], each subset consisted of three samples. The Kennard-Stone algorithm allows for finding the most representative samples from the whole set. The corresponding matrix  $F$  was calculated for potentiometric data using the following equations:

$$F_p = X_{pff}^+ X_{vff} \quad (1)$$

$$X_{pcorr} = X_{ppred} F_p \quad (2)$$

It was done for transformation of potentiometric sensor responses into voltammetric format.

Voltammetric data were transformed into potentiometric format using similar procedure:

$$F_v = X_{vif}^+ X_{ptf} \quad (3)$$

$$X_{vcorr} = X_{vpred} F_v \quad (4)$$

After the calculations described above  $X_{pcorr}$  and  $X_{vcorr}$  were used for prediction of must parameters using PLS models calculated with voltammetric and potentiometric data respectively. The MatLab code implementing these calculations is provided in Supplementary Materials. Efficiency of the correction was evaluated by calculation of the root mean square error of prediction (RMSEP) for transformed data.

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_{i,pred} - y_{i,real})^2}{n}} \quad (5)$$

### 3. Results and discussion

As it can be seen from Figs. 1 and 2a the structures of responses of the potentiometric and voltammetric sensor arrays are different. Potentiometric sensors are responding to ions in solutions. Voltammetric response curves are mainly initiated by oxidation and reduction processes at the sensor surfaces, but diffusion of ions inside of the sensing layer can also play its role. The variance structure in these two data sets is somehow similar as shown in PCA score plots for voltammetric and potentiometric data (Fig. 3). The dimensions of the plots and distribution of the samples do not match completely, but certain analogies can be observed: Cabernet and Garnacha samples are located at the extremes of PC1 axis, relative position of Tempranillo and Rufete samples is comparable in both plots, while the samples of the Mencia Regadio and Secano are close to zero and to each other along PC1. This implies that sensor responses in both cases are due to similar characteristics of the musts and are somewhat independent of the employed electrochemical techniques.

PLS regression was further employed to establish predictive models for quantitative relation of responses of sensor systems with chemical parameters of the musts. The regression parameters are summarized in Table 1.

Since multisensor systems are based on two different types of sensors they demonstrate sensitivity towards different chemical compounds. Potentiometric sensors exhibit almost no response to sugars, because sugar molecules in aqueous solution are not ionized under normal conditions. It is confirmed by low  $R^2$  values of corresponding PLS models. At the same time response of potentiometric multisensor system has shown good correlation with concentration of various acids. Parameters of the regression models based on voltammetric data show high response to sugars and phenols. It should be taken into account that PLS models were built against logarithm of concentration, since potentiometric sensors have linear correlation only in this scale and for calibration transfer dependent variables should be the same. In general, it is possible to obtain better results for voltammetric data modelling if non- logarithmic scale is employed.

Since the number of available samples was comparatively small additional measurements were taken in order to ensure statistical significance of the results. For three regression models (tartaric acid, pH, TPI) permutation testing (40 times) was performed in dependent variable vector for regression. Validation results obtained with permuted target value vectors were compared with those for original non-permuted vectors [34]. It was found that

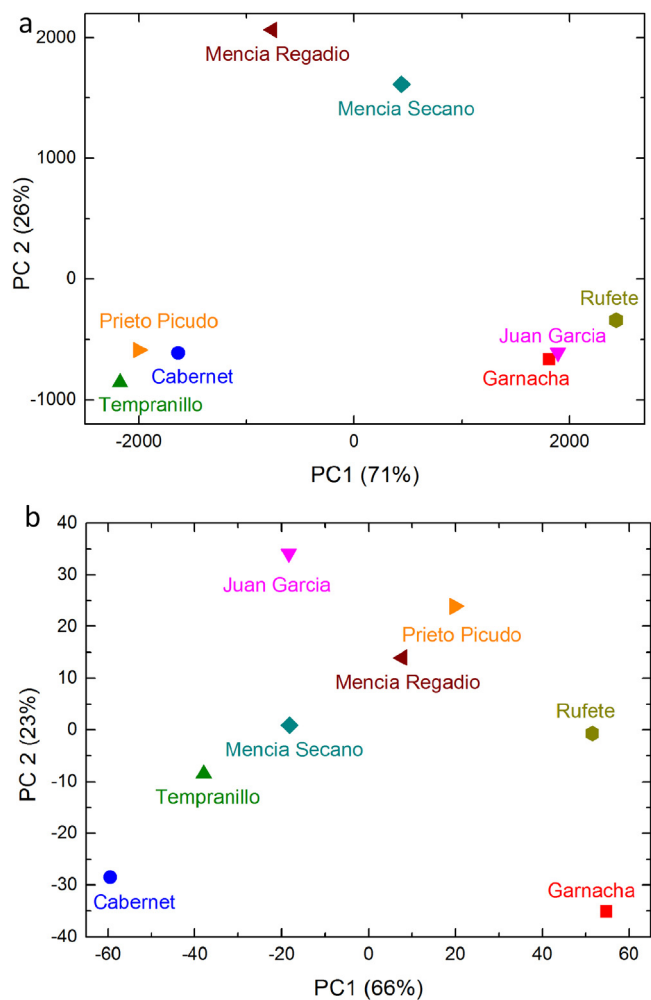


Fig. 3. Score plots of the first two components calculated for voltammetric (a) and potentiometric (b) data.

in permuted data RMSECV increased while  $R^2$  decreased significantly. In case of permutation test, the observed deterioration of the models parameters, like RMSECV and  $R^2$ , confirmed that initial correlations between dependent and independent variables were not random. The following mean values of RMSECV were obtained in 40 permutations: 0.14 log molar concentration, for tartaric acid, 0.37 units for pH, 5.49 units for TPI.  $R^2$  values were 0.13, 0.25 and 0.25 correspondently. These values confirm statistical validity of the models.

The procedure of calibration transfer obviously makes sense only when both instruments are able to determine particular parameter of interest. It means that application of the transfer algorithm is useless in case of potassium concentration, where voltammetric sensors are not responding, or for sugars where potentiometry has no sensitivity. Thus calibration transfer algorithm was applied only for three PLS models – for determination of tartaric acid, pH and TPI.

Voltammetric/potentiometric data were converted according to the DS procedure described above. 3 samples chosen by Kennard-Stone procedure were used as a transfer set. Sensor responses in the remaining samples were transformed and parameters of the interest were predicted with the potentiometric/voltammetric models.

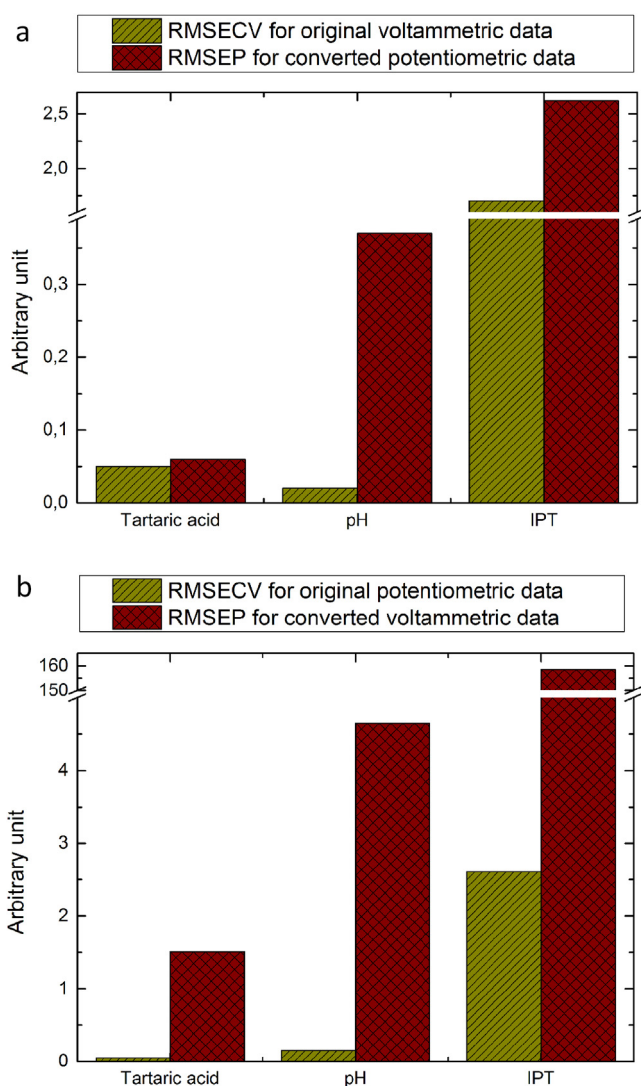
The results comprising RMSECV for original and RMSEP converted data are presented on Fig. 4(a) and (b). For better comparison raw measured and predicted values are shown in Table 1S (Supplementary materials).



**Table 1**  
Parameters of the PLS models built with voltammetric (VA) and potentiometric (PT) data.

Parameter	Range and units	Data for PLS model	RMSECV	R <sup>2</sup>	LV
Total acids	0.658–0.958; log of molar conc	PT	0.02	0.97	5
		VA	0.08	0.46	3
Malic acid	(–1.787) to (–1.587); log of molar conc	PT	0.03	0.87	2
		VA	0.05	0.68	2
Tartaric acid	(–1.6) to (–1.285); log of molar conc	PT	0.05	0.81	1
		VA	0.05	0.8	5
pH	3.17–3.96; pH	PT	0.15	0.81	1
		VA	0.02	1	5
K	(–1.567) to (–1.307); log of molar conc	PT	0.01	0.98	4
		VA	0.1	0.1	3
Brix degrees	19.8–22.8; °Bx	PT	1.25	0.1	2
		VA	0.62	0.78	1
Sugar	2.278–2.350; log of molar conc	PT	0.03	0.13	2
		VA	0.01	0.78	1
Total phenol content index (TPI)	14–27; TPI units	PT	2.61	0.72	2
		VA	1.7	0.88	5

LV – number of latent variables.



**Fig. 4.** Root mean square errors obtained with PLS models for: (a) original voltammetric and converted potentiometric data; (b) original potentiometric and transformed voltammetric data.

The calibration transfer algorithm worked rather well when potentiometric data were converted in voltammetric format. Prediction ability for tartaric acid concentration decreased only by 0.01 in logarithmic scale of molar concentration when prediction was performed from converted potentiometric data. Prediction accuracy comparable to that of the original voltammetric model was also obtained for TPI. The results of voltammetric data transformation into potentiometric format were significantly different. For all studied parameters RMSEP values derived from transformed voltammetric data have increased at least 30 times. An obvious reason for this is in the number of latent variables in the regression models for voltammetry and potentiometry. While models for potentiometry were mainly based on a single LV, five LVs were required for voltammetry.

The obtained results point out a possibility of inter-instrumental response standardization in multisensor analysis. The suggested procedure can substantially increase practical applicability of electronic tongues since it opens up a perspective of shared regression model employment by different multisensor systems. This can be of particular importance when calibration model was constructed using very large number of samples [35] and, thus, significant unnecessary efforts on re-calibration may be avoided. However, there are certain issues requiring further thorough investigation. The choice of standardization subset for transfer must follow specific procedure in order to provide for robust results – this procedure has yet to be developed and validated. Kennard-Stone algorithm employed in this study may be not optimal choice for various practical tasks. The opportunity of using synthetic samples for standardization has to be explored. This would allow avoiding the necessity to have the same real samples for standardization in complex cases. An option of measuring predefined mixture of standards looks much more attractive.

#### 4. Conclusion

At the moment, each particular multisensor system should be individually calibrated using the set of samples with known target parameters. Application of different sensor types in multisensor systems (electronic tongues) does not allow for inter-laboratory use of the same calibration model, while this would help to save tremendous efforts and resources spent for recalibration of each new sensor system and also would let to come up with generalized models valid over various systems. Another benefit would be a calibration update option, when some new samples measured on the different device can be added to the original calibration made on

primary instrument. In order to address these issues we employed the mathematical algorithm earlier suggested for calibration transfer between spectrometers and known as direct standardization. Due to the mathematics behind the calculation of transfer coefficients this method can be applied on a more general scale – as a method for transfer of calibration models between different analytical instruments having different response structure. A feasibility study of this approach was performed using voltammetric and potentiometric multisensor systems applied to the analysis of grape musts. It was shown that such transformation is possible and allows for using of e.g. potentiometric data with regression models constructed for voltammetric data. Obviously, both devices should be sensitive towards the target parameters in question. The number of latent variables in regression models describing response of two instruments must be carefully considered. Several important issues related to the choice and the number of transfer samples have to be thoroughly explored in future works.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2017.02.099>.

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### Biographies

**Maria Khaydukova** received her PhD in analytical chemistry from Saint-Petersburg State University in 2016. She started working in Institute of Chemistry of Saint-Petersburg State University since 2011 and worked as a research fellow in several research projects. Her current research interests include chemometrics, multisensor systems and their joint application as solution for different analytical tasks.

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