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Fast and Efficient Food Quality Control Using Electronic Noses: Adulteration Detection Achieved by Unfolded Cluster Analysis Coupled with Time-Window Selection

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Abstract The objective of this work is to report the improvements obtained in the discrimination of complex aroma samples with subtle differences in odor pattern, by the use of a fast procedure suitable for the cases of measurements in the field demanding decision-making in real time using a portable electronic nose. This device consists of a sensor array which records changes in conductivity as a function of time when aroma molecules reach the sensors. The core of the method consists of applying unfolded cluster analysis to selected time windows (UCATW) within the temporal evolution of the aroma profile recorded by the gas sensors, yielding an efficient, fast, and reliable data analysis tool that is easy to perform for electronic nose users. The performance of this data handling was tested in two case studies of food adulteration. The results demonstrated that this methodology enables to discriminate highly similar samples, herewith reducing the probability of achieving a wrong grouping due to the use of flawed data. The automation of this type of analysis is simple and improves the efficiency of the device significantly, herewith reducing the time of sensor's signal recording that is necessary for a reliable assessment of the studied system. The results were validated by clustering the sample component scores that are obtained by applying parallel factor analysis (PARAFAC) to the original three-dimensional data array. An additional validation was obtained by means of a leave-one-out resampling procedure.

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Introduction

The use of gas sensor arrays, known as electronic noses (ENs), has been steadily increasing since the 1990s. In the last decade, their efficiency has been significantly improved because important developments took place in the area of data handling and multivariate data analysis methods. Promoted by the advances in sensor technology, the use of ENs, both in the market research and development, has risen in fields such as food and pharmaceutics technology, process engineering, and medicine, in which noninvasive and nondestructive data handling techniques are necessary for the analysis of complex systems (Mahmoudi 2009; Peris and Escuder-Gilabert 2009; Pennazza et al. 2013; Versari et al. 2013). ENs also offer a particularly valuable feature that is being increasingly exploited: Its size, shape, and complexity can be tailored for specific applications, being one of them is the design of portable miniaturized devices. In many cases, companies and safety control offices are interested in verifying the quality consistency or the proper preservation of different batches of a product. When the differences between samples' odor patterns are expected to be very subtle, it is advantageous to run the measurements in real time, since formerly stored databases can yield inconsistent results due to sensor drifts. Thus, the availability of a user-friendly and reliable methodology of data mining is of critical importance. For instance, in the import-export commerce, controls must be applied by means of real-time monitoring procedures. To this end, a portable EN can be used to control the quality of the shipments, with the additional demand of performing a fast screening to detect any possible spoilage or adulteration as quickly as possible. This challenging task requires minimal operation time with only a limited number of samples to be examined and compared, herewith asking the operator to optimize data acquisition and analysis in order to obtain successful results.

The literature describes several different methods of pattern recognition for analyzing the data recorded with ENs (Skov and Bro 2005; Scott et al. 2006; Wang et al. 2009; Fu et al. 2012), but none of them focus on the needs and requirements arising from having to quickly detect a change in aroma pattern with only a few samples. Therefore, we present in this paper a new procedure of data analysis that relies on unfolding the "sample by sensor by time" three-way EN data together with selecting appropriate time windows within the registered sensors curves. To perform the analysis, a well-known unsupervised clustering algorithm such as *k*-means cluster analysis is used. The whole procedure will be abbreviated by the acronym UCATW. Its usefulness was evaluated by applying UCATW to two case studies that were selected to demonstrate the efficacy of UCATW for detecting subtle changes in aroma patterns: the adulteration of green coffee beans and cayenne pure samples, which in both cases is caused by incorporating a small percentage of another variety of coffee or spice, respectively.

In order to validate the new approach, a subsequent parallel factor analysis (PARAFAC) was performed, using the important time windows as identified by UCATW. PARAFAC is a data analysis technique which was used in previous EN studies (Skov and Bro 2005; Calderisi et al. 2006; Padilla et al. 2006; Chu and Ghahramani 2009); the aim of the validation is to compare the UCATW and PARAFAC results with respect to discriminating the different types of samples. In addition, the results of both methodologies were further validated by a leave-one-out resampling (LOOR) method, in order to confirm the effectiveness of the methodology and the reliability of the results.

Materials and Methods

Materials and Devices

Materials

For the coffee analysis, two green coffee bean varieties were chosen, which were kindly provided by Sibarita S.A. (Argentina): (1) Tristao Curitiva Parana and (2) Tristao Curitiva Bourbon. For the spices, cayenne and bell pepper powders were provided by Katerine S.R.L. (Argentina). Pure air (quality 4.7) was used as a baseline and for cleaning the sensors' compartment in between measurements. Headspace crimp caps with PTFE/silicone septa were provided by Agilent Technologies.

Devices

The EN prototypes that were used in our study were described in detail in previous works (Monge et al. 2004; Lovino et al. 2005; Rodríguez et al. 2010); to illustrate, a basic diagram is presented in Fig. 1a. During the measurements, the headspace aroma of the samples under study remains in the sensor's chamber for some minutes in order to allow the sensor's signal to evolve over time; this is shown in Fig. 1b, in which, for a representative sample, a plot of a typical sensor response (i.e., conductance) over time is presented. Before and after each measurement, the sensor's chamber was swept with pure air until a constant and repeatable baseline was achieved. For each sample, each 5 s, the raw sensor readings were collected and used as the input data for the analysis.

Methods

Acquisition of Data with Portable EN: Two Case Studies

Adulteration of a pure variety of green coffee beans Six grams of each sample were placed in chromatography vials sealed with crimp caps and polytetrafluoroethylene (PTFE)/silicone septa, and the odor was aspirated from the sample's headspace by a minipump (miniature diaphragm, Thomas Inc.), bringing the odor to a sensor chamber equipped with six conductimetric sensors. Three types of samples were studied. The first two types pertain to different varieties of green coffee beans: Tristao Curitiba Parana and Tristao Curitiba Bourbon, which will be denoted by C_1 and C_2, respectively. The third type is a mixture composed of 90 % of C_1 and 10 % of C_2 and will therefore be denoted by $C_{1\text{-}2}$.

Adulteration of pure cayenne with bell pepper powder About 0.1 g of each sample were placed in the sensor chamber of an EN device, which was especially designed for analyzing powders, with seven sensors. Cayenne samples will be denoted by S_1, bell pepper samples by S_2, and the mixture composed of 80 % of S_1 and 20 % of S_2 by $S_{1\text{-}2}$. Note that, because cayenne spice has a much stronger odor than coffee beans, much smaller amounts of cayenne spice need to be used to get detected by the sensors.

Data Dimension and Data Handling

Data The obtained raw data matrix with the recorded sensor's signals over time is three-dimensional: $\underline{\mathbf{X}}$ (sample × sensor × time). In order to apply the UCATW methodology, we first unfolded the three-way matrix $\underline{\mathbf{X}}$ into a two-way $I \times JK$ matrix $\mathbf{X}^{\mathbf{unfold}}$ by concatenating the different (time) slices of $\underline{\mathbf{X}}$ horizontally. Next, a *k*-means cluster analysis (MacQueen 1967; Kiers 2000) was applied to $\mathbf{X}^{\mathbf{unfold}}$.

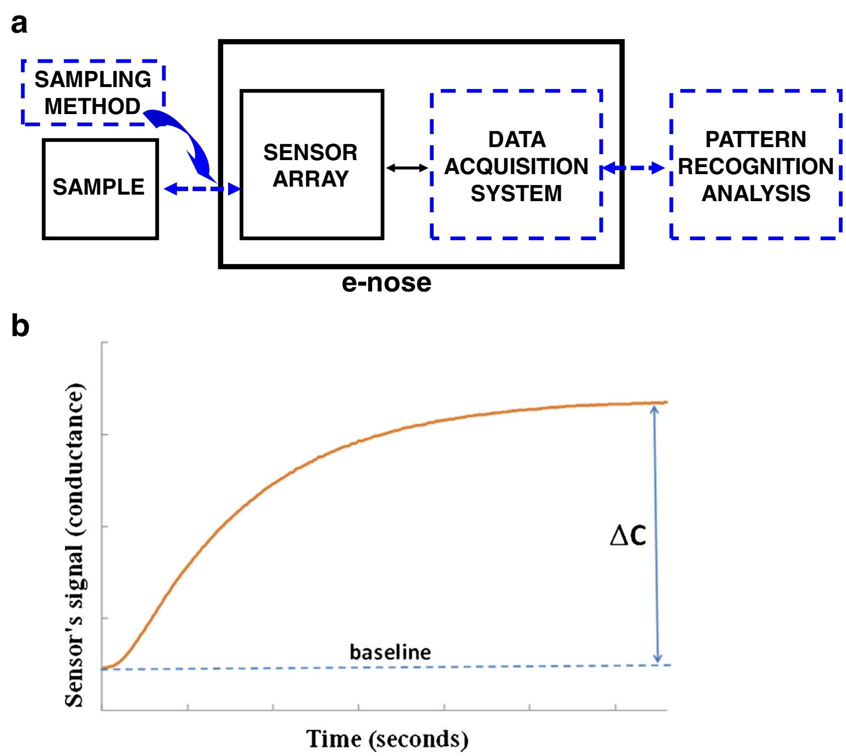

Fig. 1 **a** Diagram of the main modules of an electronic nose. The components/aspects of the technique which influence the data acquisition, type of data, and the associated data analysis are framed with *blue dotted lines*. **b** Evolution over time of a typical response of a sensor for an electronic nose device using the steady-state sampling methodology. ΔC represents the change in conductance of the sensor when detecting odors

Identifying the appropriate time window The goal of this study is to show that when an appropriate time window is selected, performing a k-means analysis on $\mathbf{X}^{\mathbf{unfold}}$ allows for a perfect separation of the different types of samples (also in the presence of adulterated samples). To determine the optimal time interval, we will try different time windows, which implies that only parts of $\mathbf{X}^{\mathbf{unfold}}$ are used and perform unfolded-CA on each time window (i.e., on the selected part of $\mathbf{X}^{\mathbf{unfold}}$).

Validation of the UCATW methodology We will validate the UCATW method in two different ways. The first way consists of applying three-way methods. In particular, we will perform a PARAFAC analysis with Q components to the three-way data matrix $\underline{\mathbf{X}}$. Next, the sample scores on the Q components are subjected to a k-means analysis. This two-step procedure will be denoted by the acronym PARAFAC-CA. The second way to validate the UCATW method is to demonstrate its stability by performing a LOOR method. In this method, each sample in turn is excluded from the data set, and the UCATW procedure is applied to the reduced data. Next, for each (reduced) data set, the correctness of the resulting clustering is evaluated.

Results and Discussion

We seek a methodology to shorten the time spent for discriminating samples in field measurements, i.e., in those cases in which there is no possibility of measuring many replicates and build a database. Thus, with a minimal number of measurements, the EN user should be able to take a decision. To test this task in such a demanding situation, we have designed two case studies, choosing two products of great importance in international trade: (1) green coffee beans (characterized by a very soft aroma) and (2) cayenne, which is a very expensive and appreciated spice.

First Case Study: Adulteration of Green Coffee Bean Samples

In order to study the influence of the selected time window on sample's discrimination, we systematically seek for the optimal time window which allows for a correct discrimination of the three types of samples. To this end, first, the number of selected time points in the unfolded matrices was increased, starting from the last point of the measurements (i.e., 1,320 s) and progressively increasing the time window toward the beginning of the measurements. In particular, different $\underline{\mathbf{X}}_{\mathbf{i}}$ were constructed by, starting with only the last time point, each time adding one more period of 5 s (i.e., 1,320, 1,320–1,315, 1,320–1,310,…, 1,320–0). Each matrix $\underline{\mathbf{X}}_{\mathbf{i}}$ is unfolded to a two-way matrix $\mathbf{X}_{\mathbf{i}}^{\mathbf{unfold}}$. Note that both $\underline{\mathbf{X}}_{\mathbf{i}}$ and the two-way matrix $\mathbf{X}_{\mathbf{i}}^{\mathbf{unfold}}$ contain information regarding the same time window. Next, the two-way $\mathbf{X}_{\mathbf{i}}^{\mathbf{unfold}}$ matrix was analyzed by k-means analysis with three clusters (i.e., there are two pure and one adulterated sample types). To validate the UCATW results on each three-way $\underline{\mathbf{X}}_{\mathbf{i}}$ matrix, a PARAFAC analysis with one component was performed. Note that the sensor data (and this for all considered time windows) adequately could be modeled with PARAFAC as more than 90 % of the variance in the data is explained by a PARAFAC model with a single component. Next, the obtained sample component scores were clustered by means of a *k*-means analysis with three clusters. Finally, for each obtained clustering (i.e., based on the PARAFAC sample component scores or on $\mathbf{X_i^{unfold}}$), the corresponding average silhouette width (ASW) value, which indicates how well the different groups/clusters are separated from each other, was computed (Rousseeuw 1987). The AWS varies between 0 and 1, the larger ASW the better the split.

In Fig. 2, for the different considered time intervals (starting with the last time point and each time increasing the time period with 5 s), the obtained results for UCATW (solid black line) and PARAFAC-CA (dashed blue line) are presented when performing a *K*-means analysis with three clusters. Note that, for the sake of clarity, only a few time intervals are marked in the figure, and the number between parentheses indicates the number of time points the time interval in question consists of. For example, when using the information from the time period 1,225–1,320 s and sampling each 5 s, 20 time points are being selected for each sensor for each sample, yielding a three-way matrix $\underline{\mathbf{X}}_\mathbf{i}$ with I=7, J=6, and K=20. When this matrix is unfolded, a two-way matrix $\mathbf{X^{unfold}}$ results with I=7 and JK=120.

The results for the UCATW analysis (solid black line) show that the ASW value, which represents the goodness of grouping, starting at 0.82 when only the last time point is used, increases when the time window becomes wider (i.e., more earlier time points are included in the analysis) until a maximum of almost 0.88 for the time interval 1,320–825. This suggests that increasing the time window starting from the last time point leads to a better discrimination of the samples. However, when more (earlier) time points are included (e.g., 1,320–625, 1,320–375), the ASW steadily decreases until a final value of 0.86 for the case where all time points are included in the analysis. Although the grouping of the samples is correct for every time interval and that all the obtained ASW values are good (considering that the best possible ASW value is 1), the ASW decreases when early time points of the sensor curves (below 800 s) are included. This suggests that, at the beginning of the measurements, the sensor signals contain information that does not help to discriminate the three different sample types from each other.

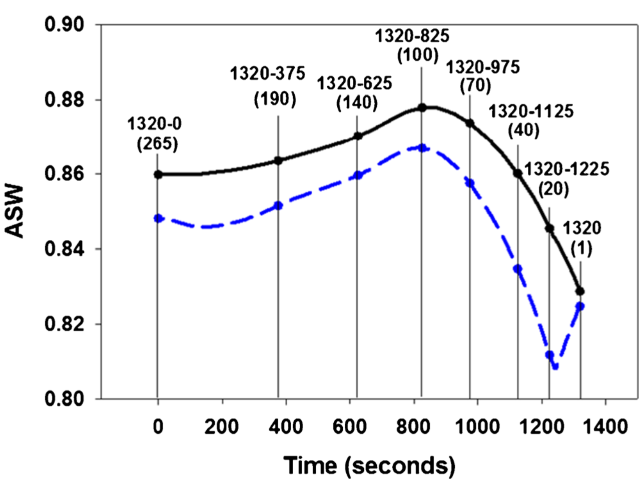

Fig. 2 ASW values for the clustering of coffee samples with three clusters obtained by (1) UCATW (*solid black curve*) and (2) PARAFAC-CA (*dashed blue curve*) analysis, when only using selected time intervals, which are obtained by starting from the last time point and extending the time window each time with 5 s. The number of time points the time period in question consists of is indicated between *parentheses* (Color figure online)

For the procedure that combines PARAFAC with *k*-means, the resulting ASW (blue dashed line) yields a very similar pattern than the UCATW methodology. Note that for the last time intervals (at the end of the measurements), the pattern of ASW values for both strategies differs a bit. A possible reason for this may be that the clustering for these time intervals is based on a low amount of data points, implying random sample fluctuations determining the result to a larger extent.

The negative influence of incorporating earlier time points in the time windows introduces a debate about which would be the optimal time window of the sensor readings to be used for data analysis. To explore this, exactly the same analysis was performed but now starting to build the $\mathbf{X^{unfold}}$ and the $\underline{\mathbf{X}}_\mathbf{i}$ matrices from the initial time point (i.e., the fifth second) and each time adding 40 time points (i.e., 200 s).

The results are shown in Table 1, in which the considered time intervals (expressed in seconds) are presented, along with the number of time points for the intervals under the study, the associated ASW values, and whether or not a correct grouping of the samples was obtained, which is the true indicator for the goodness of the cluster analysis.

Regarding the UCATW strategy, one can see in Table 1 that the first three time intervals yield fluctuating ASW values and, much more important, a wrong grouping of the samples. A correct grouping of the samples is for the first time found for the intervals 0–800 and 0–1,000. Because the interval 0–600 resulted in an incorrect grouping of the samples, it was decided to also consider other time intervals within the curve (see next rows in Table 1). From this analysis, it appears that the interval 600–800 is the first interval which, with only 41 time points, yields a good ASW value and a correct grouping of the samples. It is clear that the immediately preceding interval (i.e., 400–600 s), although having the same number of time points, does not yield a correct clustering of the samples. Moreover, also the intervals 200–400, 200–600, and 400–600 caused a wrong grouping, whereas the interval 200–800 gave a correct grouping, which is probably due to the fact that the interval 600–800 is included in the interval 200–800. Among the intervals starting at 600 s or later, different intervals are encountered that have the same (or a larger) number of data points and that also yield a correct clustering of the samples into the three underlying sample types. The highest

Table 1 Average silhouette width (ASW) value and whether or not the resulting grouping of the coffee samples in three clusters is perfect for selected time intervals

Time window		Type of analysis			
		UCATW		PARAFAC-CA	
Initial-final time (s)	Number of data points	ASW	Correct grouping	ASW	Correct grouping
0–200	41	0.85	No	0.92	No
0–400	81	0.75	No	0.76	No
0–600	121	0.79	No	0.80	No
0–800	161	0.81	Yes	0.81	Yes
0–1,000	201	0.85	Yes	0.84	Yes
200–400	41	0.81	No	0.83	No
200–600	81	0.81	No	0.83	No
200–800	121	0.81	Yes	0.81	No
200–1,000	161	0.85	Yes	0.84	Yes
400–600	41	0.80	No	0.82	No
600–800	41	0.83	Yes	0.83	Yes
600–1,000	81	0.87	Yes	0.86	Yes
800–1,000	41	0.89	Yes	0.89	Yes
800–1,200	81	0.89	Yes	0.88	Yes
800–1,320	105	0.88	Yes	0.87	Yes

The grouping of the samples is obtained by means of UCATW or PARAFAC-CA, when only considering the time points for the time intervals under study

UCATW unfolded cluster analysis to selected time windows, *PARAFAC-CA* parallel factor analysis and cluster analysis

ASW value (i.e., 0.89) with a minimal number of data points (i.e., 41) is obtained for the interval 800–1,000 s.

The validation of the UCATW results by using PARAFAC-CA yielded remarkably similar results, supporting the two-step strategy. In particular, the interval 800–1,000 s was the best time window with the same ASW value and a minimal number of data points, supporting the findings obtained by using UCATW. The only difference was the result obtained for the time interval 200–800 s in which no correct grouping of the samples was encountered. The reason for this may be that the clustering is based on the sample component scores instead of the raw (unfolded) data, with the latter containing more information regarding the clustering than the former. Moreover, the components are chosen in such a way that they explain as much variance as possible in the data and, therefore, may not retrieve the most important information regarding the clustering of the samples (Vichi and Kiers 2001; Wedge et al. 2009; Timmerman et al. 2010).

Second Case Study: Adulteration of Cayenne Samples

A second case of sample adulteration was studied by carrying out an analogous procedure with samples of pure cayenne, with bell pepper being the spice acting as the adulterant. In Fig. 3, one can see that for the cayenne samples, a steady decrease of the ASW is obtained by UCATW (solid black line) when increasing the time window from the last time point through the beginning of the measurements. However, a short time interval with steady ASW values is found at later time points (i.e., 620–720 s). Note that the total measurement time (i.e., 12 min) for the cayenne samples is smaller than for the coffee samples (i.e., 22 min), which is probably due to the stronger aroma that is released by the spices, resulting in a faster increase in the sensor signals than for the green coffee beans. The strong aroma of the spices is probably also the reason why a good discrimination of the samples is achieved at earlier time points (when starting from the initial time points). In particular, the results indicate that above 200 s, the discrimination is always correct, with very good ASW values (i.e., above 0.90) and with only a few data points being used (Table 2).

Also, in this second case study, the validation of the methodology with PARAFAC-CA yielded a similar pattern, supporting the obtained UCATW results. PARAFAC-CA analysis using one component displays slight deviations when few data points are included in the analysis, although the ASW remains high and the grouping of the samples is always correct, like in the first case study (coffee samples). In Table 2, the results for PARAFAC-CA of the selected time intervals are in line with those obtained with UCATW. The only exception is the 0–300-s interval, which shows a wrong clustering of the samples when using PARAFAC-CA. Note that a similar case is observed for the interval 200–800 for the coffee samples (see Table 2 and the "First Case Study: Adulteration of Green Coffee Bean Samples" section).

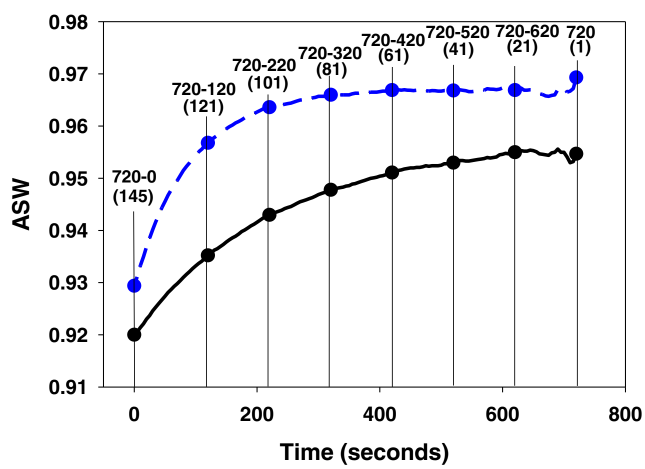

Fig. 3 ASW values for the clustering of spice samples with three clusters obtained by (1) UCATW (*solid black curve*) and (2) PARAFAC-CA (*dashed blue curve*) analysis, when only using selected time intervals, which are obtained by starting from the last time point and extending the time window each time with 5 s. The number of time points the time period in question consists of is indicated between *parentheses* (Color figure online)

Table 2 Average silhouette width (ASW) value and whether or not the resulting grouping of the spice samples in three clusters is perfect for selected time intervals

Time window		Type of analysis			
		UCATW		PARAFAC-CA	
Initial-final time (s)	Number of data points	ASW	Correct grouping	ASW	Correct grouping
0–150	31	0.77	No	0.12	No
0–200	41	0.80	No	0.00	No
0–250	51	0.81	No	−0.02	No
0–300	61	0.82	Yes	0.11	No
0–500	101	0.89	Yes	0.80	Yes
50–100	11	0.80	No	0.13	No
50–150	21	0.83	No	−0.01	No
100–200	21	0.85	No	0.21	No
200–300	21	0.90	Yes	0.90	Yes
300–400	21	0.93	Yes	0.95	Yes
350–400	11	0.93	Yes	0.96	Yes
300–500	41	0.94	Yes	0.96	Yes
400–450	11	0.94	Yes	0.96	Yes
400–500	21	0.94	Yes	0.96	Yes
450–500	11	0.95	Yes	0.97	Yes
300–720	65	0.95	Yes	0.97	Yes

The grouping of the samples is obtained by means of UCATW or PARAFAC-CA, when only considering the time points for the time intervals under study

UCATW unfolded cluster analysis to selected time windows, *PARAFAC-CA* parallel factor analysis and cluster analysis

Validation Process by LOOR

In order to add a second test of validation for the UCATW methodology, a LOOR procedure was carried out for both data sets (i.e., coffee and spice) for the selected time intervals listed in Tables 3 and 4. LOOR was also applied when using PARAFAC-CA using the same time windows (see Tables 3 and 4).

Table 3 shows the results for the validation process of the coffee samples for both methods. In the case of UCATW, the ASW values were greater than 0.75 in all the time intervals used (i.e., 0–1,320, 800–1,320, 800–1,200, 800–1,000, 600–1,000, and 600–800 s). Note that the time interval of 600–800 s has two cases which resulted in a wrong assignment of the samples (i.e., when removing C_{1a} and removing C_{1b}), and this is both for UCATW and PARAFAC-CA. In particular, one adulterated sample was wrongly assigned to one of the pure sample types, suggesting that for this time window, using only one control sample distorts the results.

In Table 4, in which the results for the spice data set are displayed, the ASW values are always higher than 0.92 in the time windows used (i.e., 0–720, 300–720, 450–500, 400–500, 400–450, and 300–500 s), with a correct assignment of the samples in all cases.

Comparison of the Results Achieved in the Two Case Studies

The two case studies were selected because they involve the difficult task of discriminating pure and (slightly) adulterated samples based on their patterns of sensor signals only. Despite

Table 3 Recovered average silhouette width (ASW) values for leave-one-out resampling procedure for selected time windows for the UCATW and PARAFAC-CA methods for the coffee samples' data set

Method	Time window	ASW removing selected samples							Correct grouping (for all the cases)
	Initial-final time (s)	C_{1a}	C_{1b}	C_{2a}	C_{2b}	$C_{1\text{-}2a}$	$C_{1\text{-}2b}$	$C_{1\text{-}2c}$	
UCATW	0–1,320	0.84	0.84	0.84	0.84	0.89	0.98	0.79	Yes
	800–1,320	0.85	0.86	0.86	0.86	0.91	0.90	0.82	Yes
	800–1,200	0.87	0.87	0.87	0.87	0.92	0.98	0.83	Yes
	800–1,000	0.87	0.87	0.87	0.87	0.92	0.98	0.83	Yes
	600–1,000	0.84	0.85	0.85	0.85	0.90	0.98	0.80	Yes
	600–800	0.75	0.75	0.80	0.80	0.86	0.98	0.75	No[a]
PARAFAC-CA	0–1,320	0.84	0.75	0.83	0.83	0.88	0.99	0.78	Yes
	800–1,320	0.85	0.84	0.85	0.85	0.90	0.98	0.80	Yes
	800–1,200	0.86	0.86	0.86	0.86	0.91	0.99	0.82	Yes
	800–1,000	0.87	0.87	0.87	0.87	0.92	0.99	0.83	Yes
	600–1,000	0.85	0.83	0.84	0.84	0.89	0.99	0.80	Yes
	600–800	0.75	0.78	0.80	0.80	0.86	0.99	0.76	No[a]

UCATW unfolded cluster analysis to selected time windows, *PARAFAC-CA* parallel factor analysis and cluster analysis

[a] One $C_{1\text{-}2}$ sample was clustered together with the single C_1 pure sample

Table 4 Recovered average silhouette width (ASW) values for leave-one-out resampling procedure for selected time window for the UCATW and PARAFAC-CA methods in the case study of spice samples' data set

Method	Time window	ASW removing selected samples						Correct grouping (for all the cases)
	Initial-final time (s)	S_{1a}	S_{1b}	$S_{1\text{-}2a}$	$S_{1\text{-}2b}$	S_{2a}	S_{2b}	
UCATW	0–720	0.94	0.94	0.94	0.95	0.93	0.92	Yes
	300–720	0.97	0.97	0.95	0.96	0.95	0.94	Yes
	450–500	0.97	0.97	0.95	0.96	0.95	0.94	Yes
	400–500	0.96	0.97	0.95	0.96	0.94	0.94	Yes
	400–450	0.96	0.96	0.95	0.96	0.94	0.94	Yes
	300–500	0.96	0.96	0.95	0.96	0.94	0.93	Yes
PARAFAC-CA	0–720	0.95	0.95	0.92	0.93	0.95	0.95	Yes
	300–720	0.99	0.99	0.96	0.96	0.96	0.97	Yes
	450–500	0.99	0.99	0.96	0.96	0.96	0.97	Yes
	400–500	0.99	0.99	0.96	0.96	0.96	0.97	Yes
	400–450	0.99	0.99	0.96	0.96	0.96	0.97	Yes
	300–500	0.99	0.99	0.96	0.96	0.96	0.97	Yes

UCATW unfolded cluster analysis to selected time windows, *PARAFAC-CA* parallel factor analysis and cluster analysis

this challenge, in both cases, discrimination of the samples using UCATW was highly successful, showing the effectiveness of the adopted method. In addition, the validation using PARAFAC-CA and the LOOR procedure supported these results.

Moreover, the UCATW analysis with varying time windows demonstrated some peculiarities of cayenne and coffee beans which pertain to the different nature of their aroma patterns. First, for the cayenne case (see Fig. 3), as compared to the coffee samples, no initial increase in the ASW value is observed when increasing the number of data points, starting from the last time point (see Fig. 2) until the time interval 1,320–825 s. It seems that the positive effect of including more data points into the analysis is counteracted by the negative influence of the sensor's data features at early time points, which is detected with high sensitivity by UCATW. In contrast, PARAFAC-CA appears not to be sensitive to the information given by the earlier time points, at least not until times shorter than 320 s are included in the analysis.

Additional Results

The application of the UCATW methodology to different time regions within the aroma recordings provided additional relevant information for the EN user. Watching the sensor curve shapes in Fig. 4 and the results depicted in Tables 1 and 2, it is evident that a correct grouping with good ASW values can be obtained when using data later than 3 min after the start of the measurements, even when some signals have not yet reached their plateau. This is highlighted in Fig. 4 in which the evolution of the response over time for each sensor is displayed, which allows a visual inspection of the different time windows under study. The areas above 600 s (coffee) and 200 s (spices) are shadowed to indicate the time region for which the analysis always retrieved the true clustering. The corresponding data are also shadowed in Tables 1 and 2.

Two comments can be outlined relating to previous work. First, our results show a different perspective than the ones reported by Wedge et al. (2009), in which it is stated that sensor readings should be considered for data analysis only when the sensors reached their equilibrium state (i.e., the plateau region). A practical consequence of our results is a significant reduction of the measurement time needed, which, in field applications, constitutes one important limiting factor in the analysis.

Second, the results confirm that the very first region, in which there is a steep increase in the response of the sensor signals, introduces some uncertainty which may impair data analysis and clustering. This observation is in line with Vilanova et al. (1996), in which it is mentioned that the first minutes of the sensor readings are unsuitable for data analysis, probably due to the inhomogeneity of the gas in the sensor chamber.

Conclusions

This work demonstrated that the new UCATW method is able to rapidly detect subtle differences between samples using only the data contained in a selected time window taken from the sensor curves using the *k*-means clustering algorithm, which is available and easy to handle for most users. In

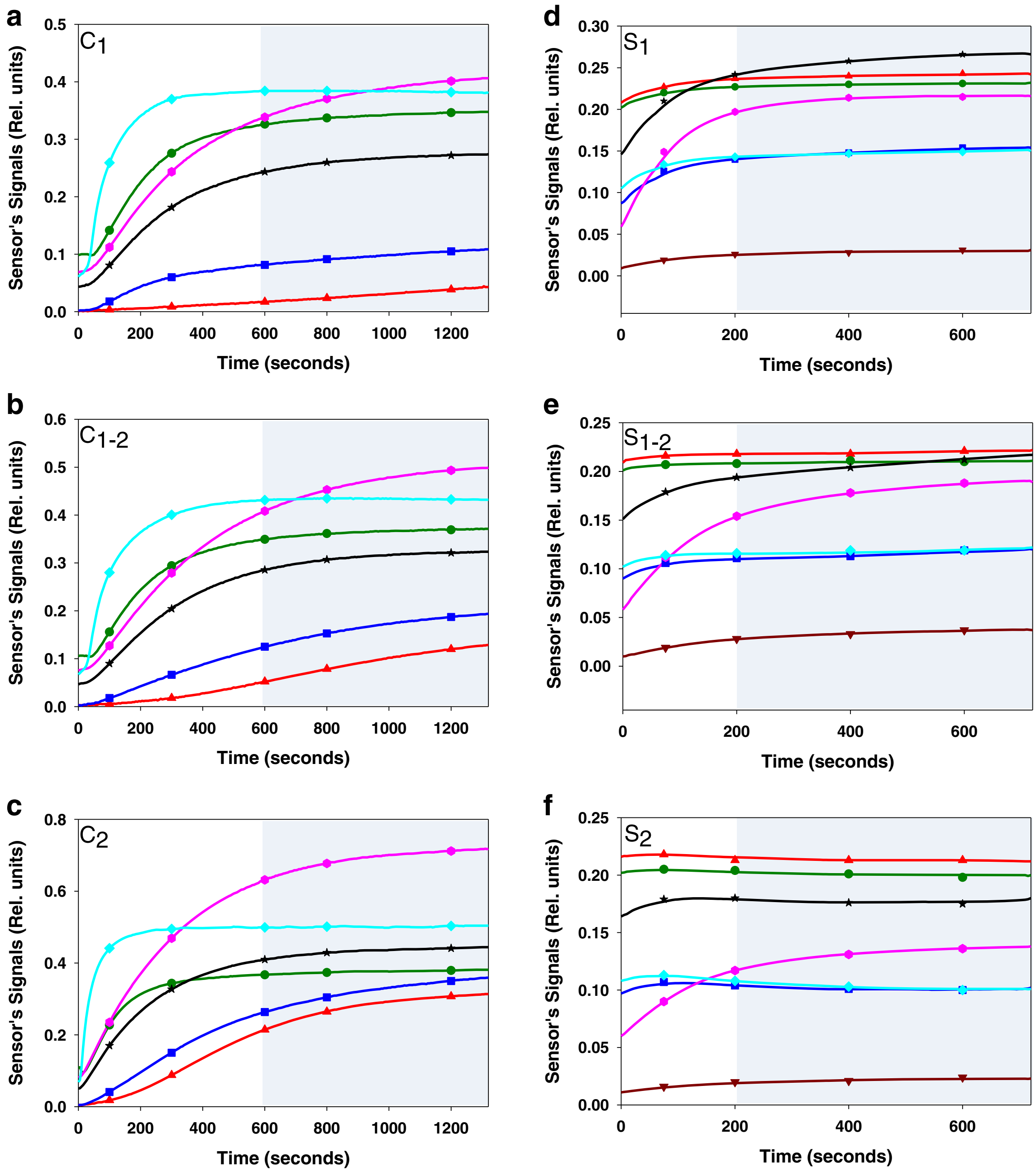

Fig. 4 Evolution and comparison over time of the sensor signals for pure and adulterated samples ($C_{1\text{-}2}$; $S_{1\text{-}2}$). The *shadowed region* represents the zone for which a perfect grouping of the samples into the three sample types is always obtained when analyzing increasing time windows, starting from the last data point, by means of either UCATW or PARAFAC-CA. Sample types are the following: **a** sample C_1, **b** adulterated sample $C_{1\text{-}2}$, **c** sample C_2, **d** sample S_1, **e** adulterated sample $S_{1\text{-}2}$, and **f** sample S_{2fs}

addition, two remarkable features were found which help in improving the performance of the data analysis when using ENs. First, UCATW demonstrated that it is not necessary to wait until the sensor signals reach their plateau, which is an advantageous feature when fast measurements are needed. Second, by using the UCATW method, it was clear that the very first minutes of the measurements are not reliable enough to be included in the data analysis because they may cause erroneous groupings.

In summary, this work presents an alternative for the data analysis associated with ENs, putting the emphasis on the use of unsupervised methods, and enabling the implementation of fast and real-time measurements with a portable EN in field applications that requires an immediate response.

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Conflict of Interest Silvio D. Rodríguez declares that he has no conflict of interest. Diego A. Barletta declares that he has no conflict of interest. Tom F. Wilderjans declares that he has no conflict of interest. Delia L. Bernik declares that he has no conflict of interest. This article does not contain any studies with human or animal subjects.

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