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Electronic nose and chiral-capillary electrophoresis in evaluation of the quality changes in commercial green tea leaves during a long-term storage

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ABSTRACT

Electronic nose and capillary electrophoresis were applied in quality control of green tea samples subjected to long-term storage. Twelve representative green teas were considered, available as an "aged" (tea leaves stored during a long-term period of two years) and/or "not aged" (fresh products) samples. Their infusions were analyzed by an electronic nose, equipped with an array of six metal oxide semiconductor (MOS) sensors to obtain olfactive fingerprints of the volatile compounds in the infusions headspace. Upon training and chemometric analysis of acquired data (linear discriminant analysis), the electronic nose was found to be able in correctly classifying unknown samples as "aged" or "not aged". Concomitantly, the infusion samples were analyzed by Cyclodextrin-modified Micellar Electrokinetic Chromatography (CD-MEKC) for determination of catechins. The analysis of seven most represented catechins and the methylxanthines theobromine and caffeine revealed a general loss of the polyphenols in each of the considered aged samples (up to 45%, w/w). In addition, the applied enantioselective method based on (2-hydroxypropyl)-β-cyclodextrin (HP-βCD) as chiral selector, was exploited for the estimation of (+)-Gallocatechin in the presence of (−)-Gallocatechin; the latter, as the non-native enantiomer, can be associated to the epimerisation of (−)-Epigallocatechin and was assumed as a marker occurring in case of uncorrected storage conditions of tea leaves. Interestingly, it was observed that epimerization did not significantly occur during aging. The application of CD-MEKC and electronic nose allowed for a fast characterization of green teas taking into account that the aroma is a decisive parameter for the acceptance of the product, whereas the catechins content is associated to the biological value.

1. Introduction

Tea is the second most widely consumed beverage in the world after water and its regular intake is associated with improved human health. In particular, green tea is obtained by the leaves of *Camellia sinensis* (L.) Kuntze steamed immediately after harvesting; this process provides enzymes deactivation with the consequent preservation of polyphenols from oxidative degradation. The unique polyphenol composition of green tea is thus mainly comprised of monomeric catechins that have been found to play a role against cancer, cardiovascular diseases and other degenerative diseases [1–3]. Although the sales growth of green tea in the recent years can be attributed to the increase of health-oriented consumers, the tea flavor still remains the most contributory factor to the popularity of the product [4]. The recognition of odor quality and intensity of food components can be carried out by aroma extract dilution analysis (AEDA) based on gas chromatographic analysis of food extracts using olfactometric detection [5,6]. The AEDA method has been applied to the identification of odorants in green tea by preliminary steam distillation under reduced pressure of a relatively high amount of tea leaves, and the subsequent concentration of the distillate by using adsorptive columns [7–9].

An alternative approach is represented by the so-called "blind" or "fingerprinting" procedures, in which a complex instrumental signal is elaborated to obtain a comprehensive, multivariate description of the sample (fingerprint), rather than specific chemical/physical information. For instance, the electronic nose

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technique has been conveniently applied in tea's quality control by means of the direct headspace analysis of leaves or their infusions. In a pioneering work, an electronic nose equipped with metal oxide semiconductor (MOS) sensors was efficiently used in classifying black tea aroma and flavor at different processing stages [10]. More recently, MOS electronic nose was employed for the identification of geographical origin of black tea [11] and for the rapid estimation of the quality grade of green tea in terms of aroma [12–16], showing the high potential of this technology in tea classification and quality monitoring. Nevertheless, none of these studies was addressed to the evaluation of the quality changes occurring during long-term storage of green tea leaves. This subject has been previously studied focusing on the variations of the non-volatile components. In particular, Friedman et al. evaluated by HPLC analysis the loss in catechins content in green tea leaves over a six-month storage, showing the considered catechins degraded with time mainly during the first two months, although no identification of transformation/degradation products was attempted [17].

In the present study, infusions prepared using commercially available green teas were analyzed in order to evaluate the effect of a very long-term period (two years) of storage of the tea leaves, under home-like conditions. In particular, the attributes that were considered as highly qualifying from both the commercial and biological point of view were the catechins content and the aroma. Catechins were analyzed in the obtained infusions by means of micellar electrokinetic chromatography (MEKC) carried out under chiral conditions, in order to selectively detect (−)-Gallocatechin and (−)-Catechin, two non-native catechins whose presence can be associated to the epimerisation of (−)-Epigallocatechin and (−)-Epicatechin, respectively, occurring during manufacturing processes or uncorrected storage conditions of fresh products [18–20]. Concomitantly headspaces generated from the same tea infusions were analyzed by means of a MOS-based electronic nose to monitor changes in the volatile organic compounds (VOCs) that contribute to the aroma upon aging. In particular, the characteristic olfactive fingerprint of each sample was acquired and, upon training and data elaboration by means of a chemometric approach, unknown samples were analyzed and classified.

2. Material and methods

2.1. Materials

Catechin standard references (±)-Catechin hydrate ((±)-C), (+)-Catechin ((+)-C), (−)-Epicatechin (EC), (−)-Epigallocatechin (EGC), (−)-Epicatechin gallate (ECG), (−)-Epigallocatechin gallate (EGCG), (−)-Gallocatechin ((−)-GC), (−)-Gallocatechin gallate (GCG), Caffeine (CF), Theobromine (TB), sodium dodecyl sulfate (SDS) and (2-hydroxypropyl)-β-cyclodextrin (HP-βCD, degree of substitution ~0.6) were from Sigma-Aldrich (Milan, Italy, www.sigmaaldrich.com). (+)-Gallocatechin ((+)-GC) was from Molekula (Germany, www.molekula.com), syringic acid, was from Fluka (Buchs, Switzerland, www.sigmaaldrich.com). Boric acid, phosphoric acid, sodium hydroxide, and all the other chemicals of analytical grade, were purchased from Carlo Erba Reagenti (Milan, Italy, www.carloerbareagents.com). Water used for the preparation of solutions, tea infusions and running buffers, was purified by a Milli-Q apparatus (Millipore, Milford, MA, USA, www.millipore.com). The analyzed tea samples were obtained from Grosserbe s.r.l. (Bologna, Italy).

2.2. Apparatus

The EOS835 electronic nose (Sacmi Imola s.c.a.r.l., Imola, Bologna, Italy, www.sacmi.it) was employed, comprising a sampling apparatus (including a pump, electro-valve, and electronic flowmeter), a thermally controlled sensor chamber (35 cm^3 internal volume) containing an array of six different thin film MOS chemical sensors, and the software Nose Pattern Editor (NPE) for data handling, preprocessing and analysis. The used sensors and their main attributes were reported in the literature [21].

The headspace was transported to the sensors chamber at a 150 $cm^3\ min^{-1}$ flow. The sensors chamber temperature was set at 55 °C, while the MOS sensors temperature was singularly set at temperatures ranging from 350 to 450 °C, as suggested by the manufacturer. Data sampling was carried out every second using a 1000 mV voltage. For each sample, sequences of 15 cycles of exposure were performed, each consisting of 0.3 min of “before” (flushing reference air to measure the baseline signal), 0.3 min of “during” (adsorption phase, exposing the sensors to the sample), 5 min of “after” (desorption phase, flushing reference air to allow sensors to return to their baseline value of resistance) and 1 min of “wait” (flushing reference air before the following measurement cycle). Experiments were repeated on each sample in different days.

Electrophoretic experiments were performed by a $HP^{3D}CE$ instrument from Agilent Technologies (Waldbronn, Germany, www.agilent.com). The data were collected on a personal computer, equipped with the software HPCE version A 09 (Agilent Technologies). Fused-silica capillaries (50 μm id, 30 cm total length, and 8.5 cm length to the detector) were from CM Scientific Ltd (Ryefield Way Silsden, UK, www.cmscientific.com). The separations were performed at a constant voltage of 15 kV and the cartridge temperature was 25 °C. The detection was carried out by using the on-line DAD detector and the quantitation was performed at the wavelength of 200 nm. Hydrodynamic injections were performed at 25 mbar for 5 s. New capillaries were conditioned by flushing sequentially 1 M sodium hydroxide, 0.1 M sodium hydroxide and water in the order, for 10 min each. Between the injections the capillary was rinsed with 0.1 M sodium hydroxide, water and running buffer for 3 min each.

2.3. Solutions

Borate-phosphate buffer used as the background electrolyte (BGE) was prepared at a concentration of 12.5 mM and pH 2.5 by following a standard procedure. The running buffer solution was obtained by dissolving SDS (90 mM) and HP-βCD (25 mM) in the BGE.

2.4. Calibration graphs and sensitivity

According to a previous method [19,22], the calibration was carried out for the catechins: EC (5.0–300.0 μg/mL), (+)-C and (−)-C (0.3–50.0 μg/mL), EGC (10.0–300 μg/mL), EGCG (20.0–600.0 μg/mL), ECG (5.0–150.0 μg/mL), GCG (5.0–50.0 μg/mL), (−)-GC and (+)-GC (1.0–50.0 μg/mL), and for the methylxanthines CF (10.0–500.0 μg/mL) and TB (1.0–100.0 μg/mL), in the concentration ranges given in brackets. The linearity of the response was evaluated by analyzing mixed standard solutions of the analytes in the presence of syringic acid as internal standard (100 μg/mL). Triplicate injections were made for each calibration point and the ratios of the corrected peak area (area/migration time) of the analyte to internal standard were plotted against the concentration of each of the analyzed compounds. Determination coefficients higher than 0.9990 were obtained proving an excellent response linearity. Limits of Detection (LOD) and Limit of Quantification (LOQ) were determined by diluting standard solutions till a signal-to-noise ratio of 3:1 and 10:1, respectively, was achieved. In analysis of (+)-GC and (−)-GC, the found LOD and LOQ values were 0.4 and 1.0 μg/mL, respectively; for all of the other compounds the LOD and LOQ values were 0.1 and 0.4 μg/mL, respectively.

2.5. Electronic nose data analysis

The data set acquired with the electronic nose was first subjected to features extraction employing the "many contiguous points" algorithm of NPE software, which calculates the value of resistivity for each sensor at 13 different characteristic points of the response curve, thereby obtaining 78 variables for each sample. Pattern recognition analysis was performed by means of the Parvus statistical software packages [23]. In particular, after a preliminary data scaling (column autoscaling), the extracted features were used as inputs for principal component analysis (PCA) [24] for data exploration and reduction. Subsequently, the first two components extracted by PCA were used to function as input for the linear discriminant analysis (LDA) to classify the green tea samples according to their state of conservation.

2.6. Tea samples

The analyzed tea samples were from different geographical origin, as reported in Table 1. To prepare infusions, the leaves were pulverized and 1.0 g of the powder was suspended in 50 mL of deionized water pre-warmed at 85 °C and incubated for 5 min. In analysis by capillary electrophoresis, the samples were cooled to room temperature and filtered through a 0.45 μm RC Econofilter (Agilent Technologies); the samples were then diluted (1:1) with the internal standard solution (syringic acid 100 μg/mL) prior the injection. In the case of electronic nose experiments, the samples were centrifuged for 5 min at 3000 rpm. Then, 5 mL aliquot of supernatant was collected and transferred in a glass container (volume 40 mL, provided with a pierceable rubber septum) and left in oven (5 min at 70 °C). Measurements were performed by dynamic headspace using an automated sampling system.

Table 1
Green tea samples, geographical origin and number of replicated analysis by e-nose.

Green tea	Origin	"Aged"	"Not aged"
Bancha Green	Japan	10	10
Kokeicha Green	Japan	10	10
Genmaicha	Japan	–	10
Bancha Green	Japan	–	10
Gyokuro Asahi	Japan	10	–
Sencha Ariake	Japan	10	–
White Monkej	China	–	10
Special Gunpowder	China	–	10
Li Zi Xiang	China	10	10
White Monkej	China	–	10
Chung Mee	China	10	–
Dong Yang Dong Bai	China	10	–

3. Results and discussion

3.1. Electronic nose analysis

The flavor of tea, due to the combination of hundreds of VOCs and non-volatile organic compounds present in the leaves, defines the quality grade of the products that is determined traditionally by human test panel. In the last decade, electronic nose has become an attractive technology in quality control and process operations in the food industry [25] and a number of applications for determination of tea quality have been reported [12–16]; most of these studies deal with identification of geographical origin and/or estimation of quality of tea. In the present investigation, the VOCs response to the electronic nose was used for the discrimination of the quality changes of aroma after long-term storage of tea samples of different geographical origin, selected to cover a wide range of products commercially available on the Italian market. It is widely expected that the effect of aging on tea aroma occurs in a relatively short storage times. However, since the history of the samples found on the market was not known (the packing date was not reported), we chose to compare samples declared as newly imported, with the same kind of products after a significantly long storage (two years) under home-like conditions. In details, the tea leaves were stored in the original packages at room temperature, in the dark for two years. Thus, the observable differences in aroma of the obtained infusions would only be ascribed to the effect of aging rather than to the uncertainty and bias of the actual date of manufacture.

From the literature it is known that elevated temperatures (85–100 °C) promote the highest release of organic compounds, from the leaves to the solution [26], thus also according to the conventional brewing procedure, infusions of the tea leaves were prepared by extraction of 1.0 g of the product with 50 mL of deionized water at 85 °C for 5 min.

Olfactive fingerprints were obtained by the electronic nose analysis, and then data were elaborated by chemometric approach to obtain the best discriminatory ability between the two classes of samples defined as "aged" (stored two years under home-like conditions) and "not aged" (newly imported on the Italian market). First, significant features were extracted from the sensor signals. Indeed, each sensor signal is composed of a large number of datapoints that are highly correlated, thus requiring a feature extraction operation, aimed at obtaining from the temporal evolution of each sensor signal a number of synthetic descriptors to be used in any successive computations. Preliminary experiments were performed to compare different features extraction procedures, all of them available in the NPE software, in terms of discrimination ability between two different classes.

For this purpose, a tea sample from Japan (Bancha Green) at two different storage grade, herein defined as "aged" and "not aged" was considered. Three different algorithms available on the

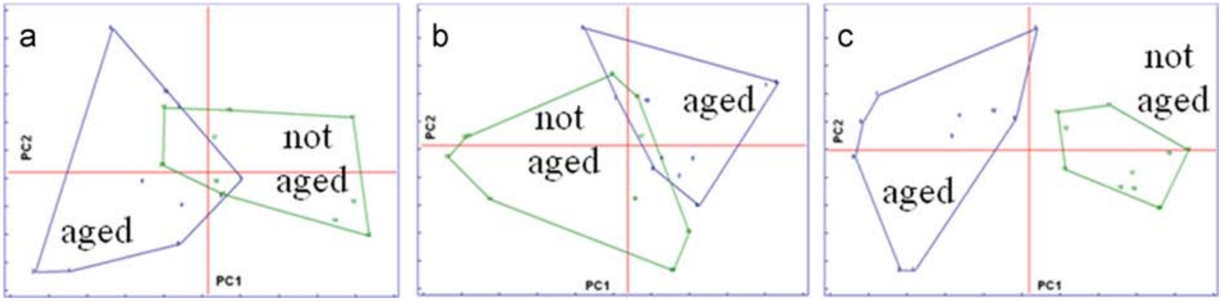

Fig. 1. Score plot of the first two principal components for an "aged" and a "not aged" Japanese green tea using as algorithm for the features extraction of the data set (a) *phase integral*, (b) *delta* and (c) *many contiguous points*.

NPE for the features extraction of the data set were evaluated, namely:

– "Delta", a classical and very simple feature: difference between the minimum sensor resistance value during the adsorption step (*R*, corresponding to the lowest peak of the response curve) and the resistance value in reference conditions (*R*0).

– "Phase integral", containing both dynamic and steady-state information on the sensor response: closed area determined by the plot of the "state graph" of the measure in the phase space, i.e. the space formed by the sensor response and its first time derivative ($x=R$; $y=\mathrm{d}R/\mathrm{d}t$) [27].

– "Many contiguous points", a rather simple way to take into account the signal evolution over time: resistance value at 13 characteristic points of the sensor response curve, starting at the first point of "during" step and sampling every 5 s for the following 60 s.

Table 2
Cumulative variance, classification ability and prediction ability percentage values in PCA and LDA analysis.

Samples	PCA	LDA	
	Cumulative percentage of PC1 and PC2 (%)	Classification ability (%)	Prediction ability (%)
"Aged" and "not aged" Chinese green teas	87	97	100
"Aged" and "not aged" Japanese green teas	87	98	100
"Not aged" Chinese and Japanese green teas	79	100	100
"Aged" Chinese and Japanese green teas	90	77	90

Each of the features was used as PCA inputs. As shown in Fig. 1, the algorithm "many contiguous points" yielded a better visual separation of classes in PCA projections compared to the other algorithms, achieving a percentage of variance explained for the first two principal components, of 84%. For this reason, such algorithm was used for all the subsequent features extractions.

Subsequently, 150 samples of green tea were analyzed, as reported in Table 1. Upon application of the "many contiguous points" algorithm, the extracted features were first subjected to PCA, which was employed to extract meaningful information from data (e.g. the ability of the electronic nose to discriminate the examined samples) and to reduce data dimensionality, the two principal components with the greatest weight being retained in the final model. PCA is a very well-known unsupervised method used for visual grouping of samples [24] and it is one of the most popular pattern recognition algorithms employed in electronic noses applications. Subsequently, linear discriminant analysis (LDA) was applied as a supervised method, in order to classify the green tea samples according to the state of conservation. To reduce the number of variables, LDA was always applied working on the scores of the first two principal components, which contain useful information and eliminate the redundant information. To validate each model, a cross-validation process with four cancellation groups was employed. In particular, the samples were randomly divided into four groups and the analysis was repeated four times, each time employing one of the four sample groups as the prediction set. With this process, each sample was classified

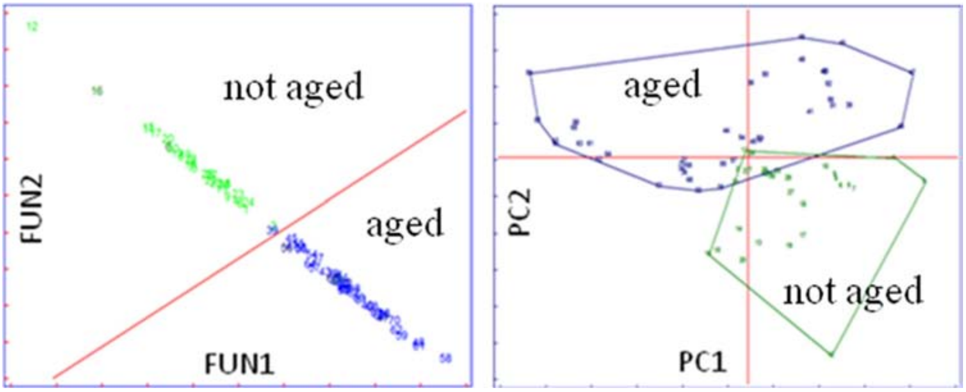

Fig. 2. LDA (left panel) and PCA score plot (right panel) analysis of "aged" and "not aged" Chinese green teas.

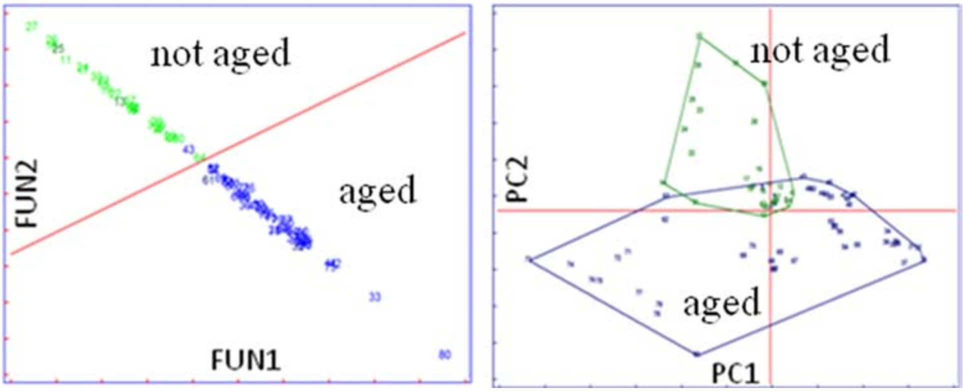

Fig. 3. LDA (left panel) and PCA score plot (right panel) analysis of "aged" and "not aged" Japanese green teas.

three times and predicted once. Table 2 summarizes all the results obtained by chemometric data analysis.

The results of the whole set of measurements are reported in Fig. 2 (green teas from China) and Fig. 3 (green teas from Japan). Right panels represent the scores of the samples on the first two principal components (overall explained variance was 87% in both cases). In both cases, a satisfactory separation between the two classes of green tea ("aged" and "not aged") is shown. The LDA results, shown in left panels, yielded a correct classification rate of 97% and 98% for China and Japan samples, respectively; while a 100% correct prediction rate was obtained in both cases. It can be observed that in both cases the models afforded good results as regards both classification and prediction, and showed to be very stable since the prediction capacity was very close to that of classification. These results clearly show that electronic nose is very suitable and a powerful tool in the evaluation of the loss of VOCs in tea leaves over a long term period.

The same results were also analyzed in order to evaluate the ability of the electronic nose to classify the samples with respect to their geographical origin (China or Japan). In this case, results obtained from "aged" samples were treated separately from those obtained for "not aged" ones. As shown in Fig. 4, it was observed that, due to the loss of characteristic VOCs, the ability of the electronic nose analysis to clearly distinguish between tea samples based on their geographical origin was significantly reduced upon aging of tea samples, thus confirming the reduced quality of "aged" tea samples with respect to "not aged" ones in terms of aroma. In particular, LDA analysis of the data obtained for the "not aged" teas (left panel) produced a classification ability of 100% and a prediction ability of 100%, demonstrating the excellent opportunity offered by the electronic nose analysis in discriminating green tea samples on the basis of the geographical origin. On the other hand, as shown in Fig. 4 (right panel), LDA analysis of the data obtained for the "aged" samples resulted in limited classification (77%) as well as prediction ability (90%). Interestingly, this observation suggests that the electronic nose analysis aiming at classification of the geographical origin of green tea samples can provide reliable results only when applied to fresh samples.

3.2. CD-MEKC chiral analysis

The biological value of green tea is undoubtedly associated to the level of monomeric catechins; in addition the caffeine content is considered to be important in defining tea quality because of the stimulating effect. In the present investigation, the quantitation of catechins and methylxanthines was carried out by using a previously optimized and validated MEKC method based on the use of

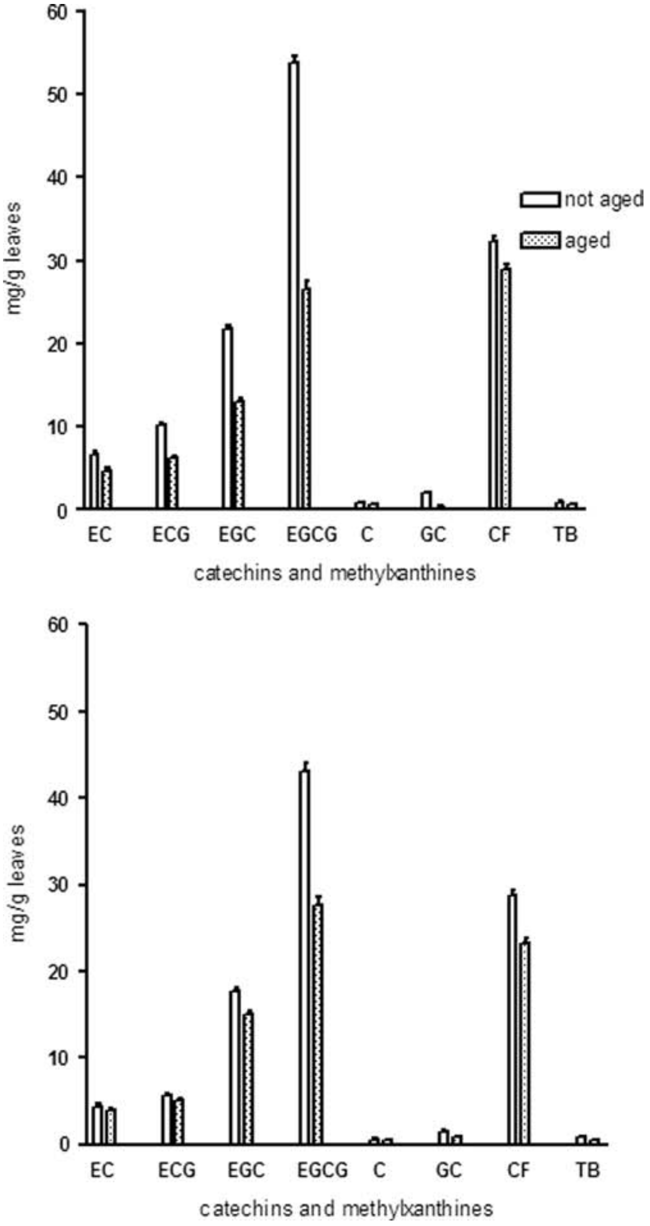

Fig. 5. Bar graphs of the catechins and methylxanthines content in "aged" and "not aged" green tea samples: Chung Mee (A) and Gyokuro Asahi (B). The analysis was performed by the described CD-MEKC (see Section 2); each of the samples was analyzed in triplicate.

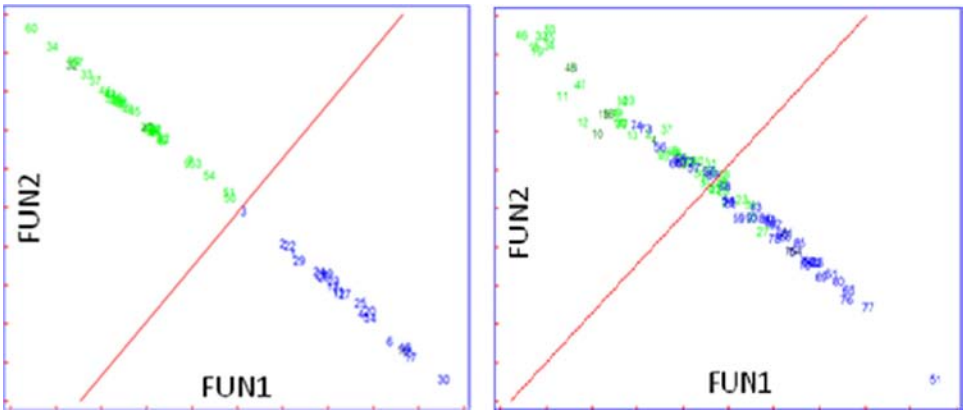

Fig. 4. LDA analysis of "not aged" (left panel) and "aged" (right panel) Chinese and Japanese green teas.

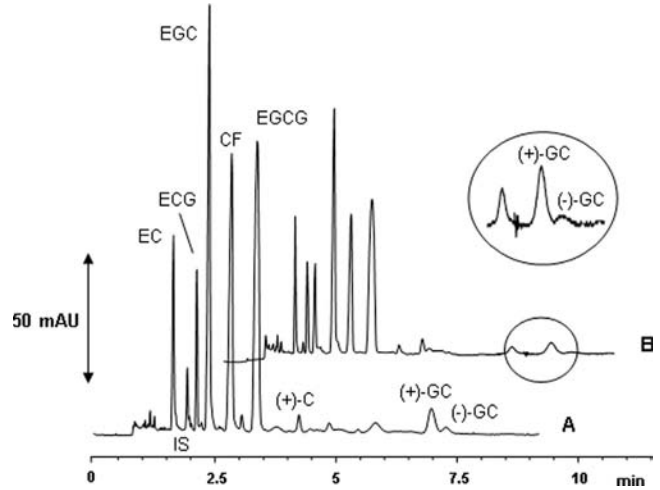

Fig. 6. CD-MEKC electropherogram of the infusion from (A) “not aged” and (B) “aged” Genmaicha green tea sample. Separation conditions: 25 mM borate-phosphate buffer (pH 2.5) supplemented with SDS 90 mM and HP-βCD 25 mM. Fused-silica capillary (50 μm id, 30 cm total length, and 8.5 cm effective length). Voltage 15 kV; temperature 25 °C. Hydrodynamic injection at 25 mbar for 5 s. Detection at 200 nm. Symbols: (+)-Catechin, (+)-C; Epicatechin, (EC); Epigallocatechin, (EGC); Epicatechin gallate, (ECG); Epigallocatechin gallate, (EGCG); Caffeine, (CF); Syringic acid (the internal standard, IS).

SDS as the surfactant (90 mM) in the presence of 25 mM HP-βCD as a chiral additive, in a borate-phosphate buffer at pH 2.5 [19,22].

In particular, the electrophoretic method was applied in analysis of tea infusions obtained from “not aged” tea samples with the aim to compare the results with those of the analysis of “aged” tea samples of the same type. The previously listed green teas were considered for the analysis of the most abundant catechins, caffeine and theobromine. In the bar graphs of Fig. 5 it is reported the comparison of catechins and methylxanthines content in “not aged” and “aged” representative samples (Chung Mee and Gyokuro Asahi). As it can be seen the level of catechins undergoes to a significant loss depending on the sample type (about 27 and 45% of the total catechins content for Chung Mee and Gyokuro Asahi, respectively) and catechin type. In a previous study dealing with the stability of green tea catechins in tea leaves, it was shown that the catechins content significantly decreased during the first two months of storage and then remained almost constant; interestingly, for relatively longer storage, the catechins levels were observed to increase [17]. This result, also observed in our study for some of the analyzed samples, was explained by taking into account that the found catechins levels were expressed as mg/g on the tea leaves regardless the humidity content; thus obviously the obtained data are affected by the loss, during storage, of volatile ingredients, including water associated with tea ingredients. For this reason and also because the history of the storage conditions of the selected samples was not known in details, our attention was focused on the variation of the enantiomeric ratio of catechins. In particular, the applied CD-MEKC method was optimized to be enantioselective for (±)-C and (±)-GC. In our previous studies it was demonstrated that (−)-C and (−)-GC are non-native enantiomers that can be yielded by epimerization of the natural occurring (−)-EC and (−)-EGC, respectively, as due to thermal treatment and/or improper storage conditions of the food containing catechins [18,19,28]. In Fig. 6 it is reported the electropherogram of Genmaicha green tea infusion at the two different storage degree (“aged” and “not aged”). As it is shown in the inset, non-native(−)-GC was detected in both the conditions, suggesting that the original sample could have been thermally treated. In addition, a significant decrease of (−)-EGC content (from 24.9 ± 1.92 mg/g to 12.7 ± 0.98 mg/g, $n=3$) was observed during the storage, however the enantiomeric ratio calculated as the native (+)-GC versus non-native (−)-GC, was found to slightly increase from “not aged” (82:18) to “aged” (84:16) sample, suggesting that epimerization to non-epicatechins should not be considered a major pathway in tea leaves. The same observations were extended to all the analyzed samples; thus, also according to previous reports on *Theobroma* beans [20], the loss of catechins could be mainly ascribed to oxidation and dimerization reactions [17,19,29].

4. Conclusion

In this work, we have developed an original methodology for the quality control of green tea samples subjected to a long-term storage, based on electronic nose analysis and chiral capillary electrophoresis. The combination of the results obtained by the two applied methods allowed for a fast characterization of green tea samples from the Italian market. In particular, it was found that the quality of tea significantly worsens with time both from the point of view of the aroma, and the biological value. The proposed approach is very simple to be performed and its reliability makes it useful for applications at manufacturer level, taking into account that the green tea aroma is a decisive parameter for the acceptance of the product by the consumers, whereas the catechins content is associated to its biological value.

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