Spectroscopic fingerprint of tea varieties by surface enhanced Raman spectroscopy

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Abstract The fingerprinting method is generally performed to determine specific molecules or the behavior of specific molecular bonds in the desired sample content. A novel, robust and simple method based on surface enhanced Raman spectroscopy (SERS) was developed to obtain the full spectrum of tea varieties for detection of the purity of the samples based on the type of processing and cultivation. For this purpose, the fingerprint of seven different varieties of tea samples (herbal tea (rose hip, chamomile, linden, green and sage tea), black tea and earl grey tea) combined with silver colloids was obtained by SERS in the range of 200–2000 cm^{-1} with an analysis time of 20 s. Each of the thirty-nine tea samples tested showed its own specific SERS spectra. Principal Component Analysis (PCA) was also applied to separate of each tea variety and

different models developed for tea samples including three different models for the herbal teas and two different models for black and earl grey tea samples. Herbal tea samples were separated using mean centering, smoothing and median centering pre-processing steps while baselining and derivatisation pre-processing steps were applied to SERS data of black and earl grey tea. The novel spectroscopic fingerprinting technique combined with PCA is an accurate, rapid and simple methodology for the assessment of tea types based on the type of processing and cultivation differences. This method is proposed as an alternative tool in order to determine the characteristics of tea varieties.

Keywords Tea · Fingerprint · Silver nanoparticles · Sers · PCA

Highlights

- Spectral measurements are performed in order to obtain tea fingerprints with SERS. Silver colloids are used to provide signal enhancement.
- The PCA tool is used to discriminate seven tea kinds (black, earl grey, linden, chamomile, rose hip, sage, and green tea).
- Leading tea adulteration since fingerprints of types of tea are successfully separated from each other.

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Introduction

Tea, a product made from the leaf and bud of the plant *Camellia sinensis*, is reported to be the most commonly consumed beverage in the world after water and has come into prominence as an agricultural product (Chen et al. 2007; Ferruzzi and Green 2006; Nie and Xie 2011). It is prepared via hot water infusion of the leaves of *Camellia sinensis* L. and has been used in China for thousands of years (Fraser et al. 2013). Generally, tea plants are consumed in three forms based on the tea manufacturing (fermentation) process: unfermented (green tea), semi-fermented (oolong teas), and fermented (black and pu-erh or red) (Kim et al. 2011; Zhu et al. 2002; Zuo et al. 2002).

Tea contains a wide variety group of compounds such as polyphenols, alkaloids, free amino acids, proteins, catechins, and vitamins. The amount of these compounds can differ depending upon the fermentation process and the degree of

fermentation. Polyphenols are believed to be bioactive components and represent antioxidant activity. Antioxidant activities among all tea types show differences due to the different tea processing methods. For example, the quantity of catechins in green tea is higher than in black tea and oolong tea since green tea is a non-fermented product (0 % degree of fermentation) (Alaerts et al. 2012; Ananingsih et al. 2013; Zhang et al. 2013). Kim et al. (2011) reported a decrease at the level of flavanols, flavonoid glycosides and caffeine and an increase in the levels of thearubigens, theaflavins and most volatiles with an increase in fermentation level especially once the fermentation levels were 20 % or greater. Besides the processing, other factors such as region of cultivation, climate type (temperature, humidity, light, and wind) and harvest time (Alaerts et al. 2012; Ma et al. 2011) may affect the amount of these compounds as well. Chemical compositions, quality, amount of active ingredients of tea types are related to all of these differences and reflect their fingerprint profile.

A number of conventional methods have been used to determine the characteristic profile of tea such as High Performance Liquid Chromatography (HPLC) to analyse the flavanols and phenolic acids in the fresh young shoots of tea (Yao et al. 2004); HPLC–mass spectrometry (MS)/MS profiling of proanthocyanidins in teas (Fraser et al. 2012); capillary electrophoresis to separate and quantify tea constituents (Sang et al. 2011); multi-spectral imaging technique and support vector machine to image texture for the sorting of tea categories (Wu et al. 2008); gas chromatography (GC) coupled with MS (GC–MS) and HPLC–MS for fingerprinting (Deng and Yang 2013). Although these techniques have been used extensively with the advantages of good repeatability, wide applicability, and reasonable qualitative and quantitative capabilities, they have some drawbacks (Deng and Yang 2013). The main disadvantage of these techniques is that they are time consuming (chromatography typically takes 30–60 min), laborious and may require a large amount of environmentally unfriendly chemicals; also the increased requirements for sample handling during preparation can adversely affect the quality of the analysis (Di Anibal et al. 2011; Yao et al. 2013).

In this field, major compelling factors are the highly complex and unknown composition of herbs and the lack of unique markers. Identification based on a restrictive number of markers is not always sufficient and could be replaced by information originating from the whole fingerprint, i.e. a characteristic profile of the herb (Alaerts et al. 2012). Instead of focusing on a limited number of compounds to obtain a global assessment of herbal products, fingerprint technology has been performed for the identification and quality evaluation of the herbal products (Dumarey et al. 2008). Fingerprints can be defined as the characteristic profile visualized the complex chemical composition of the analyzed sample and can be

obtained by spectroscopic, separation (commonly chromatographic) and electrophoretic techniques (Tistaert et al. 2011).

As an alternative method, Surface enhanced Raman spectroscopy (SERS), which is readily available, runs for less than five minutes with power signals (Panarin et al. 2010; Zhu et al. 2011; Temiz et al. 2013). In addition, when the metallic nanostructures are used at the single molecule level with Raman scattering, they increase the Raman cross-section by about 14 orders of magnitude (Kneipp et al. 1999). This enhancement provides the in situ detection of molecules with high sensitivity (Temiz et al. 2013). SERS is a well-established instrumentation with the advantages of little or no sample preparation (Cialla et al. 2012; McNay et al. 2011; Yazgan et al. 2012). Besides that, compared with other techniques, it is simple to use with high sensitivity, low operational cost, and no need for trained personnel (Güven et al. 2012; Temur et al. 2012). Therefore, SERS has become the cornerstone of many selective and ultra-sensitive detection methods in chemical and biological applications (Liu et al. 2011; Yao et al. 2013). On the other hand, SERS is defined as combining the fingerprint specificity and potential single molecule sensitivity (Cialla et al. 2012). This technique enables fingerprint spectra of the molecules to be obtained which include detailed information about the molecular composition and chemical structure of the molecules (Temiz et al. 2013) and obtains characteristic vibrational fingerprints of molecules (Yao et al. 2013). Chemical content assessment and quality control, as an important approach for determining the whole composition of teas, remains a challenging matter. Beyond the main-decision on the characteristic assessment, there is a need for improved rapid, sensitive, accurate and robust techniques without the need for trained personnel.

The aims of this study were to differentiate the discrimination of the fingerprinting pattern of different tea samples (black tea, earl grey tea and herbal teas (green tea, rose hip tea, chamomile tea, linden tea, and sage tea)) and determine the adulteration in tea samples. For this reason, a rapid and simple spectroscopic fingerprinting method was developed using SERS to differentiate the each tea varieties and the collected spectral data were analysed with PCA.

Materials and method

Tea samples

Various natural and commercially available tea trademarks of seven different kinds of tea samples including two different kinds of fermented tea (black and earl grey) and five different kinds of herbal tea samples (green tea, sage tea, linden tea, rose hip tea, and chamomile tea) were purchased in the form of tea bags for processed tea and dried fruit or tea leaves for herbal tea samples from a number of markets in Turkey.

Synthesis and characterisation of silver colloids

Silver colloids were synthesized as described by Leopold and Lendl (2003). Hydroxylamine hydrochloride ($\text{NH}_2\text{-OH HCl}$, 98.0 %, Sigma Aldrich, MO, USA), silver nitrate (AgNO_3 crystal extra pure, Merck, Darmstadt, Germany) and sodium hydroxide (NaOH , J.T. Baker, Deventer, Holland) were used as received. Solutions of NaOH (3.3×10^{-3} M) and AgNO_3 (0.01 M) were prepared with distilled water. Briefly, 1.5×10^{-4} mol of $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added into 90 ml of NaOH solution, followed by the addition of freshly prepared AgNO_3 solution (10 mL) to prepare the particle solution (1X). Once the solution was prepared, it was stored for 15 min in the dark to prevent any oxidation. In the preliminary experiments, different concentrated colloids were prepared by centrifugation of 1X and the best signal was obtained with 10-times concentrated colloid (10X) during SERS measurements. Therefore, 10X silver colloid solution was used throughout this study. Optical absorption spectra of synthesised AgNPs were collected using the Agilent 8453 UV–Vis spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) with a photodiode array detector. Transmission electron microscopy (TEM) analyses were performed on a JEOL 2100 HRTEM instrument (JEOL Ltd., Tokyo, Japan). TEM samples were prepared by pipetting 10 μL of nanoparticle solution onto TEM grids that were then allowed to stand for 10 min.

Preparation of tea infusions

Total of 39 (32 commercial and 7 natural (pure collected) tea samples (black, earl grey, green tea, sage tea, linden tea, rose hip tea, and chamomile tea) were examined. Detailed information of commercial tea samples is summarized in Table 1. Each of the 39 tea samples was brewed with drinking water. Tea infusions were prepared with 2 g of tea leaves and 100 mL of hot water at 100 ± 0.5 °C in a beaker and stirred continuously. After 30 s of brewing, 1 mL of tea liquor sample was taken and percolated with filter paper. The experiment was done in triplicate.

Table 1 Detailed information on commercial tea samples

Tea Sample	Number of sample	Origin	The size of the tea leaf (g)	Addition of another ingredient
Earl grey tea	3	Turkey	2	None
Green tea	5	Turkey	1.6–2	None
Black tea	6	Turkey	2	None
Sage tea	5	Turkey	1–1.3	None
Linden tea	3	Turkey	1.5–1.6	None
Chamomile tea	4	Turkey	1.3–1.5	None
Rose hip tea	6	Turkey	2	Okra flower

Raman spectroscopy and SERS measurements

Raman spectra were obtained with a DeltaNu Examiner Raman Microscopy system (DeltaNu Inc., Laramie, WY, USA) with a 785 nm laser source and a cooled charge-coupled device (CCD, at 0 °C) detector. Samples were prepared using the following formula for the SERS measurements; 50 μL of sample solution and 75 μL of silver AgNPs. The analysis solution was immediately placed into the Raman spectroscopy system. Spectra were obtained in the range of 200–2000 cm^{-1} at a resolution of 2 cm^{-1} . Optimised measurement parameters were integration time (with 20 s acquisition time) and baseline correction which was performed for all of the measurements at 100 mW laser power level. All measurements were done in triplicate for each tea sample.

Principal component analyses

Principally to determine systematic variation in the data matrix and in order to form groups using (dis)similarity between the seven tea types (black tea, earl grey tea, green tea, sage tea, linden tea, rose hip tea, and chamomile tea), a chemometric method, PCA, was used. Before processing the data, pre-processing techniques (mean centering, smoothing, median centering, baselining, and derivativisation) were applied to the raw data. For this reason, tea samples were categorised into two groups: fermented (black) and non-fermented (green) tea samples were evaluated in the first group, while herbal tea samples were evaluated as in the second group. Every commercial tea type was combined with its natural form as a reference of their natural references and the pre-processing was applied to commercial tea in the presence of natural tea types. Favourable outcomes of pre-processing were chosen for data analysis with the PCA model. Data processing was performed using PCA with Stand-alone Chemometrics Software (Version Solo 7.0 for Windows 7, Eigenvector Research Inc., Wenatchee, WA, USA). The multivariate method PCA allowed us to show systematic variation in a data matrix X and was also used to improve the model. The acquired data were used for obtaining the PCA model (Uysal et al. 2013).

Result and discussion

Characterisation of silver colloids

The morphology of the synthesised silver colloids was characterised by using UV-vis spectroscopy and TEM. Fig. 1 shows representative TEM images of AgNPs. The results showed that hydroxylamine-reduced silver nanoparticles were spherical in shape. Under the fabrication conditions, the

Fig. 1 TEM micrograph of silver colloids

average diameter of the silver colloid particles was estimated to be in the range of 45 nm size distributions with stable dispersions. According to the procedure described by Leopold and Lendl (2003), the colour of the hydroxylamine-reduced silver colloids differs from greenish grey to milky grey if the particle size changes from mono-disperse to poly-disperse. The silver colloids synthesised in this study had a greenish grey colour, which shows that the particles were in the mono-disperse form; this was also confirmed by UV-visible spectroscopy.

SERS spectra of tea samples and silver colloids

SERS spectra for each tea sample (10X AgNPs and tea extract) were measured in the range of 200–2000 cm^{-1} using determined experimental parameters and are shown in Fig. 2. It was obvious that AgNPs cause little or no interference with the observed SERS spectrum for the fingerprint of tea samples in the range of 200–2000 cm^{-1} . The results showed that the characteristic SERS signal of tea samples had become visible in the presence of silver colloids which

Fig. 2 The spectra of tea samples, AgNPs and tea sample couple with AgNPs (a: 10X Ag NPs, b: earl grey tea, c: black tea, d:green tea, e: earl grey tea with AgNPs, f: black tea with AgNPs, g:green tea with AgNPs) (offset 4000 a.u.)

played a keyrole as an advantage of AgNPs, as well as the perfect enhancement in obtaining significant and sharp SERS signals. Taking this into account, the SERS signal of different kinds of tea samples in the presence of silver colloids was investigated and is shown in Fig. 3.

Observable fingerprints of each tea sample were obtained by SERS measurements using 10X concentrated AgNPs; the results are shown in Figs 1S (a, b, c, d, and, e). Overall, at the qualitative and quantitative levels, the spectra were very similar. These figures include the fingerprint of both commercial and natural (pure collected) tea samples. In general, each fingerprint of a specific tea variety differed from each other regardless of their natural (pure collected) or commercial availability. The SERS spectra were identical for each tea variety, with different SERS intensities. As seen in Fig. 1Sa, sage tea samples had the same spectral fingerprint, which is specific for sage, and this was different to that seen for linden (Fig. 1Sb) or other tea varieties (Fig. 1Sc, d, and e). In contrast, some quantitative differences were observed between all herbal teas, such as linden and chamomile tea samples. Both of these have the same specific SERS bands that are visible at wavenumber of 466 and 725 cm^{-1} but the intensity of linden tea at these wavenumbers was higher than intensity of chamomile tea (Fig. 1b and c). As a result, even though, they can involve same specific SERS band, their SERS intensity may change based on amount of the different chemical bonds. This also confirms the study of Horžić et al. (2009) who reported the total identified flavan-3-ol contents of herbal linden tea sample was nearly six-fold higher than chamomile tea samples. In addition, the SERS spectrum of green tea samples had a number of sharp bands compared to the other four tea types. Green tea had a specific band at 482 cm^{-1} (C = O out of bending) (Fig. 1Sd) while other tea samples (rose hip,

Fig. 3 SERS spectrum of commercial and natural (pure collected) tea varieties in the presence of AgNPs (n: natural tea, c: commercial tea, 1: sage, 2: chamomile, 3: linden, 4: rose hip, 5: green, 6: earl grey and 7: black tea)

chamomile and linden tea samples) had this specific band almost at the noise level. Also, the intensity of specific bands of green tea had higher power levels than that of the sage tea. On the other hand, the observed specific spectrum for rose hip tea had a lower power level compared to others (Fig. 1Se). Herbal tea samples prepared from leaves had sharper SERS bands and power intensities, except rose hip tea. This may be a result of the preparation of the rose hip tea, since it was prepared from the fruit of the rose hip, while the others are prepared from the leaves. Thus, the amount of compounds extracted from fruit during brewing can be less or vice versa. This situation can create the observable SERS band diversities seen in rose hip tea. Depending on the variety, the region of cultivation and other factors may play important roles on the content of herbal tea and the chemical bonds as a result of higher/lower SERS intensities or direct sharp bands.

Herbal tea samples, black (fermented tea) and earl grey (fermented tea + bergamot oil essence) teas were also examined and the SERS spectra of both commercial and natural (pure collected) black and earl grey tea samples are shown in Fig. 1S (f and g). SERS spectrum of black and earl grey tea samples mostly demonstrated similar bands with different SERS intensities at specific bands. Also, the intensity of specific SERS bands of earl grey tea was higher or close to the intensity of black tea SERS bands. SERS spectra of black (fermented) and green tea (non-fermented) are presented in Fig. 4. The process difference based on the fermentation was presented in the spectroscopic fingerprinting method using SERS. The bands which belong to both black and green tea samples, at 487 cm^{-1} (which probably arise

from the $\delta(\text{C}-\text{C}-\text{O})$ deformations), 527 cm^{-1} , 637 cm^{-1} and 725 cm^{-1} (C-H stretching) have different intensities; in particular, the intensity of black tea was lower. For instance, the bands of earl grey tea at 527 cm^{-1} , 637 cm^{-1} , 725 cm^{-1} , 1234 cm^{-1} (C-O stretch double ester unsaturated) and 1320 cm^{-1} (vibration of monounsaturated benzene ring)

presented the spectrum of black tea samples (Fig. 4). In addition, these specific band intensities in the earl grey and black tea spectra were close to each other. Earl grey tea is composed of black tea and the essence of bergamot oil, which is acquired from the rind of bergamot orange (*Citrus aurantium* ssp bergamia) (Finsterer 2002). The amount of major flavouring substances such as linalyl acetate, linalool, and limonene changes after hot water infusion (Orth et al. 2013). Although, no difference was observed for the fingerprints of earl grey and black tea samples due to the bergamot aroma that is found in the earl grey tea, as expected, the difference was highlighted by PCA.

The same batch of leaves, when treated with different levels of fermentation, have different contents; it was reported that the tea content of flavanols, flavonoid glycosides and caffeine decrease, particularly once fermentation levels achieved 40 % or greater. Also level of thearubigens, theaflavins and most volatiles increase at the fermented level of 20 % and above (Fraser et al. 2013). The other obvious visible differences between tea types appeared on the intensity of bands related to tea components. These appeared to be present in higher quantities of the total identified flavan-3-ol contents especially EGCG in non-fermented tea than fermented (black) tea except GC and ECG (most abundant in black tea) (Horžić et al. 2009), with the former displaying higher SERS for these bands. Therefore, as shown in Fig. 4, non-fermented tea (green tea) bands had higher power SERS intensities than fermented tea (black tea) at 487 cm^{-1} , 527 cm^{-1} , and 637 cm^{-1} wavenumbers. Non-fermented tea contains more catechin than fermented tea. However, not all non-fermented teas (green tea) had higher catechin contents than fermented teas, which provide better quality, i.e. a higher catechin content of tea leaves suggested use for preparing the black tea (Dejaegher and Heyden 2013). The high intensity of the band at $725 \pm 10\text{ cm}^{-1}$ in the black tea spectrum obtained in this study can be explained by the rich catechin content of tea as a result of the C-H stretching of benzene at $735\text{--}765\text{ cm}^{-1}$ wavenumber (Workman 2001). Integration of the bands derived from the spectra for each tea type confirm the above differences in the composition of green tea, with higher intensity values based on the C-H stretching. In addition the oxidation products (theaflavin and thearubigin) of catechins found in black tea as a result of fermentation were not presented in green tea. This may resulted in missing bands at 1234 cm^{-1} and 1320 cm^{-1} (C-O stretching) for green tea samples.

When natural (pure collected) tea samples were compared with commercial tea samples, the SERS spectra of natural (pure collected) tea samples were similar to those of commercial tea samples. Both showed predominantly the same specific SERS bands, as expected, and there were little or no difference in the wavenumbers of specific bands. Only the intensity changed since all of the tea samples can be produced under different cultivation, processing time, and climate conditions. Moreover, the experienced tea maker, or 'tea

Fig. 4 SERS spectra of black and green teas using with AgNPs

master' has a key role to play in the quality of the green tea (Fraser et al. 2013).

Discrimination of different kinds of tea samples by developed PCA techniques

The spectral data of thirty-nine tea samples in seven categories were used for the multivariate analyses. A chemometric technique, PCA, was used to separate different tea samples that have no similar characteristic information. This technique can be applied for data analysis in the form of the absence or presence of pre-processing. The effect of pre-processing is shown in Fig. 5. Data processing is performed using the PCA technique; Fig. 5c shows the SERS spectra of herbal tea samples to observe (dis)similarities between the range of 200 cm^{-1} to 2000 cm^{-1} . Pre-processing (mean centering, smoothing and median centering, baselining and derivatisation) was applied to raw data to increase the performance of the PCA model and it was observed that pre-processing had a positive effect and provided discrimination between all herbal tea samples.

The distinction of herbal tea sample categorisation (chamomile, sage, linden, rose hip and green tea), was accomplished with a three-step analysis. Pre-processing techniques that provided the best discrimination are as follows: mean centering, smoothing and median centering (Fig. 5c). The mean centering operation isolated the green tea samples and rose hip tea samples from the others. The remaining three groups were exposed to a two different pre-processing steps. While the smoothing step was able to form two individual groups for the sage tea and linden tea samples, the median centering step enabled a discrete group containing chamomile tea to be separated from the others. Principal Component 1 (PC1: explained 83.84 % cumulative variance) and Principal Component 3 (PC3: explained 95.11 % cumulative variance) were used to compose this PCA model. In contrast, a two-step PCA analysis method was employed for the black and earl grey tea samples. The first pre-processing technique was baselining and the second was the first derivative step. Both baselining and derivatisation pre-processing assisted in forming two clusters, which were composed a black tea sample group and the earl grey tea sample group. Here, two groups of tea were separated from each other using pre-processing by the PCA

Fig. 5 Herbal tea samples, black and earl grey tea samples before preprocessing (a, b) and after preprocessing (c, d) in PCA model

technique (Fig. 5d). Principal component 1 (PC1; explained 84.40 % of the cumulative variance) and Principal component 3 (PC3; explained 96.94 % of the cumulative variance) were preferred for the development of this PCA model.

In Fig. 5a and b, the raw data of tea kinds with no pre-processing are presented. The raw data showed no perfect discrimination between the tea samples, while the pre-processed data exhibited perfect discrimination. Tea samples have some (dis)similarities in their structure. PCA techniques can be used to check the information of structure in the content of identification and quality control. Pre-processing reveals the information about structure. Before classification, using PCA on SERS fingerprints, tea groups were not clearly separated. However, alignment was noticeably obtained after pre-processing. It is obvious that PCA provides very good information on the (dis)similarities of tea samples. Oolong tea can be produced with young green shoots of different tea varieties. Under the same processing conditions, some oolong varieties may have similar appearances and flavour characteristics and these similar properties can cause economic adulteration. Also, expensive teas are substituted with cheaper or inferior teas so that it can be used to defraud the consumers (Lin et al. 2013). As we mentioned above, the chemometric steps involved in the SERS spectra could separate the tea kinds based on preprocessing techniques; this separation can reveal adulteration between tea kinds. The tea content may differ based on the bonds of each tea kind and the separation of each tea type can be the result of the easy detection of tea adulteration.

Conclusion

In this study, results have demonstrated that the SERS methodology is a new, robust, rapid and simple technique for the generation of fingerprint spectra of tea varieties (black, earl grey, green, rose hip, chamomile, linden and sage). This method is proposed as an alternative tool for the determination of tea characteristics. SERS can be used to specify the predominant ingredient in the tea content and construct spectral fingerprints. The chemometric method, PCA, was used for the separation of each tea variety by using different pre-processing steps and the tea varieties were categorised based on the chemometric analyses. This study was performed under ordinary conditions with little sample preparation and a very short analysis time (20 s). The other advantages of this system are its simplicity and on-site detection ability. Beyond chemical methods, SERS is a spectroscopic technique which uses silver colloids as an SERS substrate; when combined with tea samples, this provided a characteristic spectrum of tea varieties and the best signal enhancement.

The results of this study showed that SERS is capable of obtaining specific spectral data that can be used to discriminate the any adulteration that could be made in the content of

tea samples. SERS can be combined with PCA, which resulted in better discrimination of different kinds of samples. In the future, detailed studies can also be developed in terms of the adulteration of different tea samples.

Compliance with Ethical Standards This article does not contain any studies employing human or animal subjects.

Conflict of interest The authors declare that they have no conflicts of interest.

References

- Alaerts G, Van Erps J, Pieters S, Dumarey M, van Nederkassel AM, Goodarzi M, Vander Heyden Y (2012) Similarity analyses of chromatographic fingerprints as tools for identification and quality control of green tea. *J Chromatogr B* 910:61–70. doi:10.1016/j.jchromb.2012.04.031
- Ananingsih VK, Sharma A, Zhou W (2013) Green tea catechins during food processing and storage: a review on stability and detection. *Food Res Int* 50:469–479. doi:10.1016/j.foodres.2011.03.004
- Chen HX, Zhang M, Qu ZS, Xie BJ (2007) Compositional analysis and preliminary toxicological evaluation of a tea polysaccharide conjugate. *J Agric Food Chem* 55:2256–2260. doi:10.1021/jf0632740
- Cialla D, Marz A, Bohme R, Theil F, Weber K, Schmitt M, Popp J (2012) Surface-enhanced Raman spectroscopy (SERS): progress and trends. *Anal Bioanal Chem* 403:27–54. doi:10.1007/s00216-011-5631-x
- Dejaegher, B., Heyden, Y. V. (2013) Chromatographic Development, Validation and Data Handling of Tea Fingerprints. In: V. R. Preedy (Ed.) *Tea in Health and Disease Prevention* Elsevier, Amsterdam, pp 323–333. doi:10.1016/B978-0-12-384937-3.00027-6
- Deng J, Yang Y (2013) Chemical fingerprint analysis for quality assessment and control of bansha herbal tea using paper spray mass spectrometry. *Anal Chim Acta* 785:82–90. doi:10.1016/j.aca.2013.04.056
- Di Anibal CV, Ruisánchez I, Callao MP (2011) High-resolution 1 H nuclear magnetic resonance spectrometry combined with chemometric treatment to identify adulteration of culinary spices with Sudan dyes. *Food Chem* 124:1139–1145. doi:10.1016/j.foodchem.2010.07.025
- Dumarey M, van Nederkassel AM, Deconinck E, Vander Heyden Y (2008) Exploration of linear multivariate calibration techniques to predict the total antioxidant capacity of green tea from chromatographic fingerprints. *J Chromatogr A* 1192:81–88. doi:10.1016/j.chroma.2008.03.052
- Ferruzzi MG, Green RJ (2006) Analysis of catechins from milk-tea beverages by enzyme assisted extraction followed by high performance liquid chromatography. *Food Chem* 99:484–491. doi:10.1016/j.foodchem.2005.08.010
- Finsterer J (2002) Earl grey tea intoxication. *Lancet* 359:1484–1484. doi:10.1016/S0140-6736(02)08436-2
- Fraser K, Harrison SJ, Lane GA, Otter DE, Hemar Y, Quek S-Y, Rasmussen S (2012) HPLC–MS/MS profiling of proanthocyanidins in teas: a comparative study. *J Food Compos Anal* 26:43–51. doi:10.1016/j.jfca.2012.01.004
- Fraser K, Lane GA, Otter DE, Harrison SJ, Quek S-Y, Hemar Y, Rasmussen S (2013) Monitoring tea fermentation/manufacturing by direct analysis in real time (DART) mass spectrometry. *Food Chem* 141:2060–2065. doi:10.1016/j.foodchem.2013.05.054

- Guven B, Boyaci IH, Tamer U, Calik P (2012) A rapid method for detection of genetically modified organisms based on magnetic separation and surface-enhanced Raman scattering. *Analyst* 137:202–208. doi:10.1039/c1an15629b
- Horžić D, Komes D, Belščak A, Ganić KK, Iveković D, Karlović D (2009) The composition of polyphenols and methylxanthines in teas and herbal infusions. *Food Chem* 115:441–448. doi:10.1016/j.foodchem.2008.12.022
- Kim Y, Goodner KL, Park JD, Choi J, Talcott ST (2011) Changes in antioxidant phytochemicals and volatile composition of *Camellia sinensis* by oxidation during tea fermentation. *Food Chem* 129:1331–1342. doi:10.1016/j.foodchem.2011.05.012
- Kneipp K, Kneipp H, Itzkan I, Dasari RR, Feld MS (1999) Surface-enhanced non-linear Raman scattering at the single-molecule level. *Chem Phys* 247:155–162. doi:10.1016/S0301-0104(99)00165-2
- Leopold N, Lendl B (2003) A new method for fast preparation of highly surface-enhanced Raman scattering (SERS) active silver colloids at room temperature by reduction of silver nitrate with hydroxylamine hydrochloride. *J Phys Chem B* 107:5723–5727. doi:10.1021/jp027460u
- Lin J, Zhang P, Pan Z, Xu H, Luo Y, Wang X (2013) Discrimination of oolong tea (*Camellia sinensis*) varieties based on feature extraction and selection from aromatic profiles analysed by HS-SPME/GC–MS. *Food Chem* 141:259–265. doi:10.1016/j.foodchem.2013.02.128
- Liu P, Liu R, Guan G, Jiang C, Wang S, Zhang Z (2011) Surface-enhanced Raman scattering sensor for theophylline determination by molecular imprinting on silver nanoparticles. *Analyst* 136:4152–4158. doi:10.1039/C1AN15318H
- Ma T, Huang C, Meng X, Zhang Q, Zhang L, Lv X, Li J (2011) Fingerprint analysis of hawk-tea by high-performance liquid chromatography. *Food Chem* 129:551–556. doi:10.1016/j.foodchem.2011.04.059
- McNay G, Eustace D, Smith WE, Faulds K, Graham D (2011) Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS): a review of applications. *Appl Spectrosc* 65:825–837. doi:10.1366/11-06365
- Nie SP, Xie MY (2011) A review on the isolation and structure of tea polysaccharides and their bioactivities. *Food Hydrocoll* 25:144–149. doi:10.1016/j.foodhyd.2010.04.010
- Orth AM, Yu L, Engel KH (2013) Assessment of dietary exposure to flavouring substances via consumption of flavoured teas. Part 1: occurrence and contents of monoterpenes in earl grey teas marketed in the European Union. *Food Addit Contam: Part A* 30:1701–1714. doi:10.1080/19440049.2013.817687
- Panarin AY, Terekhov SN, Kholostov KI, Bondarenko VP (2010) SERS-active substrates based on n-type porous silicon. *Appl Surf Sci* 256:6969–6976. doi:10.1016/j.apsusc.2010.05.008
- Sang S, Lambert JD, Ho CT, Yang CS (2011) The chemistry and biotransformation of tea constituents. *Pharmacol Res* 64:87–99. doi:10.1016/j.phrs.2011.02.007
- Temiz HT, Boyaci IH, Grabchev I, Tamer U (2013) Surface enhanced Raman spectroscopy as a new spectral technique for quantitative detection of metal ions. *Spectrochim Acta A Mol Biomol Spectrosc* 116:339–347. doi:10.1016/j.saa.2013.07.071
- Temur E, Zengin A, Boyacı IH, Dudak FC, Torul H, Tamer U (2012) Attomole sensitivity of staphylococcal enterotoxin B detection using an aptamer-modified surface-enhanced Raman scattering probe. *Anal Chem* 84:10600–10606. doi:10.1021/ac301924f
- Tistaert C, Dejaegher B, Heyden YV (2011) Chromatographic separation techniques and data handling methods for herbal fingerprints: a review. *Anal Chim Acta* 690:148–161. doi:10.1016/j.aca.2011.02.023
- Uysal RS, Boyaci IH, Genis HE, Tamer U (2013) Determination of butter adulteration with margarine using Raman spectroscopy. *Food Chem* 141:4397–4403. doi:10.1016/j.foodchem.2013.06.061
- Workman Jr, J. (2001) Review of Interpretive Spectroscopy for Raman and Infrared. In: J. Workman (Ed.), *The Handbook of Organic Compounds* Burlington pp 211–228. doi:10.1016/B978-012763560-6/50037-4
- Wu D, Yang H, Chen X, He Y, Li X (2008) Application of image texture for the sorting of tea categories using multi-spectral imaging technique and support vector machine. *J Food Eng* 88:474–483. doi:10.1016/j.jfoodeng.2008.03.005
- Yao L, Jiang Y, Datta N, Singanusong R, Liu X, Duan J, Xu Y (2004) HPLC analyses of flavanols and phenolic acids in the fresh young shoots of tea (*Camellia sinensis*) grown in Australia. *Food Chem* 84:253–263. doi:10.1016/S0308-8146(03)00209-7
- Yao C, Cheng F, Wang C, Wang Y, Guo X, Gong Z, Zhang Z (2013) Separation, identification and fast determination of organophosphate pesticide methidathion in tea leaves by thin layer chromatography-surface-enhanced Raman scattering. *Anal Methods* 5:5560–5564. doi:10.1039/C3AY41152D
- Yazgan N, Boyaci I, Topcu A, Tamer U (2012) Detection of melamine in milk by surface-enhanced Raman spectroscopy coupled with magnetic and Raman-labeled nanoparticles. *Anal Bioanal Chem* 403:2009–2017. doi:10.1007/s00216-012-5971-1
- Zhang Y, Li Q, Xing H, Lu X, Zhao L, Qu K, Bi K (2013) Evaluation of antioxidant activity of ten compounds in different tea samples by means of an on-line HPLC–DPPH assay. *Food Res Int* 53:847–856. doi:10.1016/j.foodres.2013.03.026
- Zhu QY, Hackman RM, Ensuna JL, Holt RR, Keen CL (2002) Antioxidative activities of oolong tea. *J Agric Food Chem* 50:6929–6934. doi:10.1021/jf0206163
- Zhu Y, Dluhy RA, Zhao Y (2011) Development of silver nanorod array based fiber optic probes for SERS detection. *Sensors Actuators B Chem* 157:42–50. doi:10.1016/j.snb.2011.03.024
- Zuo YG, Chen H, Deng YW (2002) Simultaneous determination of catechins, caffeine and Gallic acids in green, oolong, black and pu-erh teas using HPLC with a photodiode array detector. *Talanta* 57:307–316. doi:10.1016/S0039-9140(02)00030-9