Determination of the chemical composition of tea by modern physico-chemical methods: a review

Abstract. Tea is internationally one of the most favored and inexpensive beverages, next only to water. More than three billion cups of tea are consumed daily worldwide and considered to be a part of the huge beverage market, not to be seen in isolation just as a ‘commodity’. Tea active ingredients are of interest to functional foods markets. Tea is a complex substance, which consists of many components and composition of tea has been researched in a wide range in the last few years. Most of the studies were performed by using chromatography methods. The review presents a summary of the latest information concerning the chemical composition of large variety of tea by different chromatographic methods, which has not previously been reviewed. Qualitative and quantitative analyses of volatile compounds, that contribute to flavor and aroma in tea composition were executed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). Low volatility organic compounds were carried out by using high-performance liquid chromatography (HPLC) methods and GC/MS. Determination of catechins and caffeine in different types of tea (green, black, oolong, pu-erh) were investigated by HPLC of the most current published researches. Exploration of tea chemical composition helps in evaluating its quality and helps to control and manage its growing, processing and storage conditions. Consequently, evaluation of tea quality does not only depend on subjective organoleptic appraisal, but also on objective physical and chemical methods with additional determination of tea components most beneficial to human health. The findings of this review are meaningful for the production of healthier teas and to help increase nutritional value of tea, ameliorate quality by supplying through developing of the growing, processing, and storage conditions.

Key words: tea, chemical composition, catechin, high-performance liquid chromatography, gas chromatography.

Introduction

Tea is the most widely consumed, popular beverage in the world next to water and prepared from Camellia sinensis plant. Composition of tea consists large amount of compounds, that significantly affect to human organism [1-2]. Tea is obtained by special treatment of evergreen tea tree leaves of Camellia sinensis. It has a very complex composition and tea leaves contain thousands of chemical compounds. Tea is typically divided into six subdivisions or types: white, green, yellow, oolong, black teas. The composition of ready-made tea depends on the origin, quality and types of fermentation. The main constituents of tea are catechins, hydroxyaromatic acids, flavonols, theaflavine, theogallins, pigments, alkaloids, sugars, amino acids, vitamins, dicarboxylic acids, cations, metal, and etc. [3].

Tea takes off fatigue and dizziness, enhances mental and physical activity, stimulates the brain, heart and breathing. Biological valuable substances in tea have a positive effect on the human body, creating a single complex. It also releases harmful substances (heavy metals, radionuclides) from the body through adsorption. The compounds of biological value in tea affect the counteracting effects on the metabolism of fats and cholesterol [5-6]. The benefits of tea, which we mentioned above, only apply to high-quality and properly maintained types of tea. And the tea we consume daily is not of high quality. Currently in our country there are 11 companies that supply tea. Due to the lack of production of tea in the country...
will be purchased about 2,500 tons of raw materials from abroad annually. The countries that import tea to Kazakhstan are India, Kenya and Russia. Almost all kinds of tea are imported from abroad and must be checked for compliance with standard requirements. Most people do not care about harmful substances contained in low-quality beverages, and consume them in large quantities. The most useful green tea become harmful and not healthy if it is made from poor quality raw materials and is not well processed. Proper collection of high quality raw materials ensures that the consumer receives the highest quality products. While collecting tea leaves, only top of the leaves is collected, leaves at the bottom are solid and can not be used as food. But over the past decades they are also being gathered. Tea of poor quality leaves is sold to third countries. Unfortunately, it is impossible to purchase tea from the best leaves in our country. A high price is not a measure of quality, on the contrary can be a source of substandard product sales at very high prices. An important part of tea leaves, as well as in finished tea, is a phenolic compound or called tannin. They not only reveal organoleptic qualities, but also show the physiological value of the drink. There are an approximately 30 000 polyphenolic compounds in tea, flavonoids are conceivably the most important group of polyphenols in tea and are the source of the many health claims surrounding tea, and specifically tea antioxidants [7; 8]. The most common flavonoids in the group are flavanols (or flavan-3-ols). Flavanoids are also referred tannins, and during oxidation are changed to theaflavins and thearubigin—the compounds responsible for the dark color and strong flavors notably present in black tea. The major flavanols in tea are: catechin, epicatechin, epicatechin gallate, galloycatechin, epigalloycatechin and epigallocatechin gallate [9-12]. Conventional tea brands have been shown to contain high levels of toxic substances such as fluorine and pesticides. Tea plants are capable of assembling large amounts of F in their mature leaves when grown on soils containing normal F concentrations, without showing toxicity symptoms. Therefore, older leaves contain a high content of fluorine, by contrast the amount of antioxidants, which increase its healing properties, decrease [13-16]. Low-priced tea products are made from such old tea leaves. It is known that a high content of fluoride in the human body can damage the bone, teeth and kidneys. Many tea leaves are not washed after leaf harvesting, thus pesticides remain in tea [17-19]. Also anthraquinone has been found in the composition of tea, which is used to protect tea plantation from birds. It was established that tea contains heavy metals such as Al, As, Pb, Cd. These metals can penetrate into tea from contaminated soil and depending on their concentrations, can have a wide range of effects on the human body.

Figure 1 – The chart of chemical composition of tea [4]

Determination of some tea components, group of phenolic compounds – tannin and caffeine according with government standards, the method based on GOST 19885-74 allows to determine in the presence of an indoxin indicator, with an oxidizer potassium permanganate. In the caffeine separation process, the material is pretreated with an aqueous ammonia solution and then heated and separated with chloroform [20]. A method for determining caffeine with HPLC from tea is also shown in GOST 10727-2013. From tea samples, caffeine is extracted with water in the presence of magnesium oxide and filtered, then determined by HPLC method equipped with an ultraviolet detector [21].

Methods

High-performance liquid chromatography

High-performance liquid chromatography or high-pressure liquid chromatography is a perspective analytical version of modern classical colonial chromatographic devices. HPLC can simultaneously detect complex samples in components, detect several components and measure the concentration of one or
more compounds (depending on the specific analytical task and standard samples). The HPLC method is used in ecological quantitative chemical analysis, sanitary-hygienic and veterinary studies, control and certification of food products and agricultural products, medicine, pharmaceutics, petrochemistry and criminology. The determination of phenolic compounds in green tea was carried out by HPLC in less than 3 minutes by rapid gradient separation. Rapid chromatographic separation was used to determine the phenolic compound and catechins in green tea and tea infusions prepared by hot water at temperatures, respectively at 90 °C, 80 °C and 70 °C, and the influence of temperature on the reduction of the main compounds in tea was examined. Together with an HPLC/MS analysis, the antioxidant capacity and total polyphenol content were measured using spectrophotometric techniques. However, the spectrophotometric techniques did not expose the degradation of catechins during staying of infusion probably due to significant antioxidant properties of degradation products [22]. Advanced glycation end products such as N-ε-(carboxymethyl)lysine (CML) and N-ε-(carboxymethyl)lysine (CEL) in tea and tea infusions were determined by liquid chromatography-tandem mass spectrometry and the data showed that the levels of CML and CEL are related to the manufacturing processes. Withering, fermentation (oxidation), and pile fermentation may facilitate the formation of CML and CEL [23]. Caffeine and catechins in tea were absorbed by a montmorillonite clay mineral adsorbent, then the concentration was determined by HPLC. This work presented that the montmorillonite adsorbent is good for caffeine and is not effective for catechin [24]. Also caffeine and catechins were allocated by sequential supercritical fluid extraction and then the concentration was determined by HPLC. The experiment was conducted at different times, pressure, temperatures, and method was optimized. However, it is not good for caffeine extraction from tea waste, but more promising for extraction of catechins [25]. Theophylline imprinted monolithic columns were designed and prepared for rapid separation of a homologous series of xanthine derivatives, caffeine, and theophylline by an in situ thermal-initiated copolymerization technique. Caffeine and theophylline were fully separated both under isocratic and gradient elutions on this kind of monolithic molecularly imprinted polymers column. Separation characteristic of monolithic MIP column was performed with a HPLC system [26]. The determination of putative chemical interactions between the milk fat globule membrane and green tea catechins was provided. In this study catechin concentrations were measured (in triplicate) by HPLC on a system equipped with a diode array detector [27]. more than 30 phenolics in tea were described by high-performance liquid chromatography-mass spectrometry methods for the rapid and routine analysis. Green and black tea infusions were injected directly onto a reversed phase HPLC column, and the phenolics eluted using two different mobile phase gradients, one optimized to resolve catechin derivatives and the other, flavonols and theaflavins [28]. 16 tea pesticides were found by the method based on matrix solid phase dispersion coupled with liquid chromatography-tandem mass spectrometry was established for the determination and the quantification of 16 pesticides in various tea [29]. Amino acids were also determined by high performance liquid chromatography with ultraviolet radiation for the rapid extraction of amino acids from tea. An accurate HPLC-UV method after derivatization using 9-fluorenylmethyloxycarbonyl chloride has been developed, validated and used to accurately and simultaneously determine 19 amino acids [30]. Green tea polyphenols extraction yield was determined using different extraction times from 10 to 60 min at 70°C, and also at different temperatures from 50°C to 100°C, keeping the extraction time constant. Also the aroma composition of different green tea samples was compared using the SPME/GC headspace methodology [31]. The effect of saccharides on sediment formation in green tea concentrate was investigated. The results show that the amount of tea sediment significantly decreased with the addition of fructose or sucrose and that the ratios of polyphenols and caffeine in the sediment sharply decreased while the proportion of total sugars markedly increased in the sediment [32].

Gas chromatography

Gas chromatography is used to separate several organic and inorganic gas mixtures, a very small number of components from the mixture can be detected and extracted. Due to the automation of the method and the shorter analysis time, gas chromatography is widely used in the continuous process in the chemical and petrochemical industries. Gas chromatography is also used in medicine, biochemistry, agrochemistry, geology, pharmacology, food production. Tea contains a large amount of volatile aromatic compounds, and the most effective way to detect these compounds are gas chromatography methods.
Phthalate esters (PAE), a group of environmental pollutants, in teas and tea infusions were quantitatively determined by a modified simultaneous distillation extraction (SDE) coupled with gas chromatography–mass spectrometry. SDE was employed as the proper extraction method for PAEs from tea samples and the extraction conditions had been optimized [33]. First information concerning (E)-nerolidol formation in tea leaves and (E)-nerolidol accumulation in oolong tea was provided [34]. A novel approach for the quantitative determination of nerolidol in teas has been developed using a headspace solid phase microextraction and a gas chromatography–flame ionization detector. The experimental parameters relating to the extraction efficiency of the HS-SPME such as fibre types, extraction temperature, extraction time, stirring rate were investigated and optimized [35]. Potent odors in roasted stem tea was determined by using GC/MS and gas chromatography–olfactometry with aroma extract dilution analysis [36]. Various instant teas produced differently from black tea were compared for their differences in volatile compounds as well as descriptive sensory analysis. Volatile compounds in tea samples were analysed by HS/GC/MS [37]. Aroma compounds from the tea infusions were detected and quantified using HS-SPME coupled with GC/MS. Sensory evaluation was also made for characteristic tea flavor [38]. Volatile collection, identification and quantification were conducted using headspace solid-phase microextraction coupled with GC/MS with some minor modifications [39].

This method is a simple method of detecting vitamin K in green tea using SPME and a flame ionizing detector with a small amount of solvent and fast results. The best analytical conditions were obtained using polydimethylsiloxane fiber [40]. Also analysis of green tea aroma compounds has been performed using the SPME/GC methodology, on a polydimethylsiloxane-coated fibre [31]. Two extraction methods, namely, solid-phase microextraction (SPME) and simultaneous distillation–extraction both followed by gas chromatography–mass spectrometry were applied for the determination of a wide range of volatile compounds in pu-erh tea. The conditions of solid-phase microextraction including fiber selections and sampling condition optimization have been previously investigated. Qualitative and quantitative differences of pu-erh tea volatile profiles were observed by applying the two aforementioned extraction methods. SDE technique achieved higher percentages of high molecular weight alcohols, acids, and esters of low volatility, whereas SPME technique was found useful for analyzing low molecular weight alcohols, methoxy-phenolic compounds, aldehydes, ketones, and hydrocarbons of high volatility that were closely related to the characteristics of pu-erh tea aroma and its sensory perception. Therefore, SPME technique was a reliable extraction method for controlling pu-erh tea quality flavor [41]. A novel strategy for objective discrimination/classification of oolong tea varieties, based on potential volatile compounds analysed by HS-SPME/ GC/MS was developed [42]. Volatile compounds from Pu-erh tea were extracted using a headspace-solid phase microextraction (HS-SPME), and analysed with a GC/MS and a gas chromatography olfactometry. The most abundant aroma components in Pu-erh tea are 1,2,3-trimethoxybenzene, followed by a-terpineol, 1,2-dimethoxybenzene and linalool oxide II in order [43]. A method for determining eight pesticide residues in made green tea as well as a tea infusion (under various brewing water temperatures: 60, 80, and 100°C) using gas chromatography (GC) micro-electron capture detector was developed and validated. The extraction method adopted the relatively commonly used approach of solid sample hydration, with the green tea hydrated before being extracted through salting out with acetonitrile followed by a cleanup procedure. The analytes were confirmed using GC-coupled to tandem mass spectrometry (GC/MS/MS) with a triple quadrupole [44]. A method for analysis of 101 pesticide residues in tea leaves was developed and validated for the first time. Pure acetonitrile was used as extraction solvent rather than acetonitrile after matrix hydration based on the amount of co-extracts and recoveries performance [45]. Linalool is a major volatile component of tea aroma was determined. A method based on HS-SPME combined with chiral GC was developed to determine R-(−)- and S-(+) -linalool in teas for the first time. To optimize the technique, the effects of various parameters on the extraction efficiency were studied comprehensively; the best extraction conditions were as follows: HS-SPME fiber, Car-boxen/divinylbenzene/polydimethylsiloxane CAR–DVB–PDMS, extraction time, 60 min; extraction temperature, 60°C. Under optimal conditions, the method showed satisfactory linearity, repeatability, detection limits, and recoveries [46].
| №  | Analyte                           | Sample preparation                                                                                                                                                                                                 | Equipment                                                                          | Link to reference |
|-----|-----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------|
| 1   | Catechins                         | The extracts were prepared from one 1 g of tea bag + 200 ml hot water at: 70°C, 80°C, 90°C. The leaching time: 4 min.                                                                                              | HPLC/MS<br>Column: C18, 50 mm x 2.1 mm x 2 μm; 40°C<br>Solvents: 0.1% HCOOH in water + 0.1% HCOOH in methanol<br>UV/VIS spectrophotometer 750 nm | 22                 |
| 2   | N'- (carboxymethyl) lysine and N'- (carboxyethyl) lysine | 40 mg of sample + n-hexane. Centrifuged at 5000g, 10 min and the n-hexane layer was removed. The residue was dried with N₂ and reduced overnight at 4 °C in a mixture of 1.5 mL of sodium borate buffer (0.2 M, pH 9.2) and 1 mL of sodium borohydride (1.0 M in 0.1 M NaOH). | LC–MS/MS<br>Column: 2.1 x 100 mm, 3.5 μm; 35°C.<br>Solvents:Aceonitrile+5 mM NFPA in Ultrapure water. | 23                 |
| 3   | Caffeine, catechins               | 100 g of sample + 1000 mL water at 80°C extracted for 8 min.160-2000 mg of montmorillonite or 32-200mg of activated carbon was added to 40 mL of the diluted green tea extract. Suspension was centrifuged 10 min, and filtered. | HPLC<br>Column: C18, 4.6 mm × 150 mm, 3 μm; 40 °C<br>Solvents: water+acetoniitre+phosphoric acid and water+methanol+acetoniitre+ phosphoric acid | 24                 |
| 4   | Caffeine, catechins               | 10 g of sample was placed in supercritical fluid extraction vessel (10, 20, 25, 30 MPa), (30, 40, 50, 60 °C) and extraction periods (1, 2, 3, 5 h) Supercriical CO₂ fluid contained different amount of ethanol as modifier (0.2; 0.3; 0.4 and 0.5 mL/min. flow rate) in 10 g/min. | HPLC<br>Column: C18 5 mm, 4.6×250 mm; 35 °C<br>Solvents :water+DMF-methanolactic acid mixture, 20:1:0.5 | 25                 |
| 5   | Caffeine, theophylline            | 5g of green tea was extracted by 150mL doubly distilled water at 50 °C, 8 h. The obtained extraction was filtered with 0.2 mm,25mm syringe filter, then it was stored in 4 °C for further work. | HPLC<br>Column: 150mm×4.0mm | 26                 |
| 6   | Catechins                         | Centrifugation of raw milk at 1030xg, 10 min, and 20 °. The raw cream was then washed three times with deionized water for 10 min, at 20 °C                                                                 | HPLC<br>Solvents: 0.1% trifluoroacetic acid in deionized water + methanol.         | 27                 |
| 7   | Catechins, flavonols, theaflavins | 18 mL of boiling water + 1 g of leaves. After 3min, the brew was filtered to remove particulate matter prior to analysis of the filtrate.                                                                           | HPLC<br>Column: C12, 4 μm 250 mm×4.6 mm; 40 °C                                      | 28                 |
| 8   | 16 pesticides                     | 0.5 g tea +100μL 2μg/g TPP, D6-dimethoate, D10-chlorpyrifos and D6-trans-cypermethrin in methanol. Homogenized with a pestle with 0.75 g C18 and 0.75 g FLS for 5 min to obtain a homogenous mixture. | LC–MS/MS<br>Column: C18100 mm×2.1 mm<br>Solvents :water+10 mmol/L ammonium acetate and methanol | 29                 |
| 9   | Amino acids                       | 100 mL boiling water + 1 g sample. Tea was brewed for 10 min on a magnetic stirrer and then filtered. For steeping time experiments, 1 g of ungrounded tea leaves was brewed up in 100 mL of hot water (90 °C) for 30, 60, 90, 120, 180, 240 and 300 s. | HPLC<br>Column: C18, 2.6 μm, 100×2.10 mm, 100 A°, C18 pre-column 4×2 mm<br>Solvents :M sodium acetate buffer 0.1 M + ACN/H2O (80:20, v/v) | 30                 |
| №  | Analyte                      | Sample preparation                                                                 | Equipment                                                                 | Link to reference |
|----|------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------|
| 10 | Catechins, aroma compounds   | 1 g of dried leaves was extracted with 20 ml of water at 70°C for 40 min. 100 mg of green tea was dissolved in 10 ml of hot water (70°C), and methylxanthines and pigments were extracted with 10 ml of chloroform. | HPLC Column: C18,4 μm 3.9 mm x 15 cm 2±3 μm 4.6 mm × 10 cm 35°C GC/MS Column: 25 m × 0.32 mm x 0.52 μm | 31                |
| 11 | Polyphenols, total sugar, catechins and caffeine | Green tea powder+ distilled water at 60 °C. Sugar (maltose, glucose, sucrose, or fructose) was added to the tea concentrate to a given concentration under magnetic stirring. | HPLC Column: C18, 250×4.6 mm 5 μm; 40 °C. Solvents: acetonitrile+acetic acid+water and acetonitrile+acetic acid+water | 32                |
| 12 | Phthalates                   | 10 g sample + 500 mL ultrapure water at 100°C. After 5 min of infusion, the solution was filtered through a stainless steel filter. | GC/MS Column: 60 m × 0.32 mm x 0.25 μm                                       | 33                |
| 13 | (E)-nerolidol                | 1 g of tea leaves were extracted with 4 mL of CH₂Cl₂ containing 5 nmol of ethyl ndecanoate as an internal standard for 8 h under dark condition. Then the solution was filtered. | GC/MS Column: 30 m × 0.25 mm × 0.25 μm                                        | 34                |
| 14 | Nerolidol                    | Ground tea powder + 20 mL boiled. Commercial SPME fibres were used in the extraction. | HS-SPME–GC Column: 30 m × 0.25 mm x 0.25 μm                                   | 35                |
| 15 | Odorants, amino acids and catechins | 260 mL boiling distilled water +6 g of sample. After standing for 45 s, the mixture was filtered. | HPLC/MS Column: C18, 250 x 4.6 mm, 5 μm Solvents: 0.1% formic acid+water tetrahydro furan and acetonitrile. | 36                |
| 16 | Volatile Compounds           | The operational conditions for continuous extractor were as follows: water inlet temperature (80-85°C), jacket temperature (80-85 °C), tea feed rate (12 kg/h), water feed rate (42 L/h), and the slope of the extractor (3-5°). | HS/GC/MS Column: 60 m × 0.25 mm × 0.25 μm                                   | 37                |
| 17 | Volatile Compounds           | 3 g tea + 150 mL distilled water for 5 min. By using a sieve, infused leaves were removed and tea infusions were transferred to glasses. | GC/MS Column:30m × 0.25 mm × 0.25 mm                                           | 38                |
| 18 | Volatile Compounds           | 3 g tea + 150 mL distilled water for 5 min. By using a sieve, infused leaves were removed and tea infusions were transferred to glasses. | HPLC Column: C18, 5 μm × 4.6 mm × 250 mm Solvents: ethanoic acid+water and acetonitrile Column: 30 m x 0.25 mm x 0.25 μm | 39                |
| 19 | Vitamin K                    | 1.5 g tea leaf + 250 mL of boiling bidistilleddeionized water. Then defined for 10 min. After this period, the tea infusions were filtered. | SPME–GC-FID                                                                     | 40                |
| 20 | Volatile compounds           | 4 g pu-erh tea+4.8 g NaCl+16 mL of distilled water + a magnetic rotor into a 100 mL vial sealed with silicone septa, which was incubated at 60 °C. | GC/MS Column: 60 × 0.32 mm, 0.25 μm                                              | 41                |
| 21 | Volatile compounds           | 10 g of dry tea sample was transferred to a 100 ml glass septum flask, and SPME fibre coated with 65 Impolylidimethylsiloxane/divinylbenzene was rapidly inserted into the headspace of the flask. | GC/MS Column: 30 m × 0.25 mm × 0.25 μm                                           | 42                |
| 22 | Volatile compounds           | 10.00 g of tea+ 30 ml boiling water, the vial was sealed with tetrafluoroethylene and immediately kept at 60°C to equilibrate for 5 min in a water bath. | GC/MS Column: 0.25 mm 0.25 μm                                                   | 43                |
| №  | Analyte                        | Sample preparation                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Equipment                                                                                                                                                                                                                   | Link to reference |
|----|--------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| 23 | 8 pesticides                   | A 20 g samples + 20 ml of water. After 2 h, acetonitrile was added and the samples were homogenized at 10,000 rpm for 5 min. +20 g sodium chloride and shaken for 30 min. Then was centrifuged for 10 min at 3000 rpm.                                                                                             | GC/MS/MS                                                                                                                                                                                                                   | 44                |
| 24 | 101 pesticides                | 5 g + 20 ml MeCN. The solution was then vortexed for 1 min. 4 g anhy-drous MgSO₄, 1 g NaCl, 1 g tri-sodium citrate dehydrate and disodium hydrogen citrate sesquihydrate was added, and the tube was vortexed to prevent coagulation of MgSO₄ for 1 min.                              | GC/MS/MS                                                                                                                                                                                                                   | 45                |
| 25 | Linalool                       | 1 g of tea + 6 mL of boiling water + 10 μL of ethyl decanoate (0.2 mg/mL, IS). The vial was immediately placed in a water bath to equilibrate for 5 min at 60°C.                                                                                                                                                                                                                                                                  | GC                                                                                                                                                                                                                         | 46                |
| 26 | Polyphenols                    | 0.5 g of tea + 50 ml of mineral water at 90°C and gently agitating under magnetic stirring for 7 min. Infusions were then filtered (43–38 lm) and diluted.                                                                                                                                                                                                                                                                                                               | ABTS [2,20-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) diaminonitritimate salt] assay DMPD (N,N-dimethylp-phenylenediamine nitrihydrochloride)                                                                                         | 47                |
| 27 | As, Cd, Cr, Cu, Hg, Fe, Pb, Mn, Zn | 0.5 g samples were microwave-digested for 30 min in a closed quartz vessel with 4 mL of HNO₃, 2 mL of H₂O₂ and 1 mL of HCl mixture. The digested solution (7 ml) was then transferred to a 10 mL decontaminated tube for its later analysis.                                                                                                                | Analyst 800 atomic absorption spectrometer                                                                                                                                                                                   | 48                |
| 28 | Polyphenols                    | 2 g of sample + 100 ml boiling water and was filtered after 1 min. using filter paper. 2 g tea + 4 g sugar +100 ml boiling water and boiling was continued for 2 min.                                                                                                                                                                                                                                                                                      | 1,1-diphenyl-2-picryl hydrazyl radical (DPPH) used widely to evaluate the free radical scavenging ability of various extracts                                                                                                                                                     | 49                |
| 29 | Polyphenols                    | For sample preparations, dilutions of the samples were carried out using deionized water and phosphate buffer (50 mM, pH 6.8) for reconstituted milk (RS) and casein (Cn), respectively.                                                                                                                                                                                                                                                                                                                           | The fluorescent probe binding method (fluorimetry analysis) and isothermal titration calorimetry (ITC) analysis                                                                                                                                                                    | 50                |
| 30 | Fluorine                       | 2000-mg sample +200 ml deionized water, boiled for 15 min, filtered after cooling. An ion-selective electrode measured the fluorine content in the four filtrates separately with the standard curve method.                                                                                                                                                                                                                                                      | Ion-selective electrode standard curve technique                                                                                                                                                                                                                                       | 51                |
| 31 | Mg, Ni, Rb, Sr, Cd, Cs, Ba, Pb, Al, Cu, U, Na, V, As, Se, Sn | Tea leaves were dried in oven at 70°C for 12 h to constant weight. The dried samples were crushed to obtain fine powder using a mortar and pestle and sieved using a 75-μm nylon mesh.                                                                                                                                                                                                                                                                               | ICP-MS                                                                                                                                                                                                                     | 52                |
| 32 | Catechins                      | 10.0 g + 300 mL boiling water for 3 min. After filtering through the silicon treated filter paper, the tea infusions were centrifuged at 10,000 g and 20°C for 45 min.                                                                                                                                                                                                                                                                 | FTIR spectroscopic measurements UV–vis spectroscopy analysis Fluorescence spectroscopy                                                                                                                                       | 53                |
| 33 | Antioxidants, color parameters | 1.00 g of +250 mL of boiling ultra-filtered water. Infusions were allowed to steep for 1 h with continuous swirling and then cooled. Subsequently, the infusions were filtered and stored at 4°C for further analysis within 8 h.                                                                                                                                                                                                                                               | ABTS [2,20-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) diaminonitritimate salt] assay DMPD (N,N-dimethylp-phenylenediamine nitrihydrochloride) ColorQuest XE                                                                      | 54                |
| №  | Analyte   | Sample preparation                                                                                                                                                                                                 | Equipment                                                                                                                                   | Link to reference |
|----|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| 34 | Theophylline | 2.0 g + 100 ml of boiling water for 3 min. It was then diluted by a factor of 1:20.                                                                                                                              | Square-wave voltammetry                                                                                                                     | 55               |
| 35 | Tannins   | 0.5000 g of tea was heated for 10 min at 90 °C in about 50 ml of deionized water, the mixture was filtered.                                                                                                           | Turbidimetric method Photometric method                                                                                                     | 56               |
| 36 | Theophylline | 5 g + 60 ml of boiling double distilled deionised water for 30 min. After filtration, the filtrate was collected into a 100 ml volumetric flask and diluted to marker.                                          | Electrochemical method based on CdSe microparticles modified glassy carbon electrode                                                        | 57               |
| 37 | Fluoride  | The method involves fusion of tea samples with 8 M NaOH at 600 °C for 30 min. The fused samples were extracted with boiling distilled water.                                                                   | SPADNS colorimetric method USEPA Method 13A                                                                                                  | 58               |
| 38 | Fluoride  | 2.000 g sample + 150 ml 100 °C deionized water and kept in a 100 °C bath for 10 min. After filtration, the volume was determined.                                                                                    | Fluoride ion selective electrode method                                                                                            | 59               |
| 39 | Fluoride  | 2 g of sample + 200 ml of de-ionized water (100 °C) and kept on water bath (100 °C) for 10 min, then cooled to room temperature, filtered, and the filtrate was brought back to 200 ml with de-ionized water. | Fluoride ion selective electrode and spectrometry.                                                                                           | 60               |
| 40 | Fluoride  | Tea bag + 100 mL boiled water. After 5 min of infusion, tea bag was taken out and cooled to room temperature. 0.5 mL of total ionic strength adjustment buffer was pipetted per 5 mL standard fluoride solutions. | Fluoride ion selective electrode and spectrometry.                                                                                           | 61               |
| 41 | Amino acids, Na, K, P, Mg, Fe, Cu, Zn, Mn, Al, Ni, Cd, Pb | 1 g of sample + hot distilled water (100 ml) was added to each beaker and the leaves were allowed to infuse for 10 min. The infusions were filtered.                | Flame photometry Spectrophotometer AAS                                                                                                    | 62               |

All the scientific articles above are taken from the ScienceDirect database. Summarizing these scientific works, the composition of tea can be formed depending on the place of its cultivation (nature, climate, altitude, etc.). In the articles 80% of tea in the study was Asian tea. Identified important constant components of tea mass, product of secondary metabolism and constitutes the bulk of tea polyphenols – catechins and their types. Also types of caffeine and amino acids, natural or artificial types of volatile compounds that affect the smell and taste of tea were determined. Analyzed harmful compounds, that reduce the quality of tea, such as pesticides, fluorine, heavy metals. Several volatile compounds contribute to the aroma of tea beverages, and are identified by GC-MS in conjunction with head-space analysis or solid-phase microextraction (SPME). GC-MS was initially used for determining the difference in aromas of different tea grades. Volatile compounds of green, black, oolong and white teas by dispersive liquid-liquid microextraction coupled with GC have been reported. The aroma of Pu-erh tea characterized using headspace – solid phase microextraction, combined with GC-MS and GC-olfactometry. HPLC is the most frequently used methods to determine catechins, alkaloids, theaflavins, and thearubigins in teas. HPLC is also used to determine phenolic acids (such as gallic and caffeic acids, etc.), flavonols (such as quercetin, kaempferol, and myracetin), lignans, triterpenoid saponins, pigments (chlorophyll and carotenoids) in tea. The detection of heavy metals and fluorine was carried out using electrochemical methods and atomic absorption spectroscopy (AAS), flame AAS, inductively coupled plasma mass spectrometry. Methods for analytical analysis have been developed and optimized methods have been shown for sample preparation.
Conclusion

This paper presents chromatographic methods for determining the composition of the tea component and shows several useful aspects of this technique. New modern methods for studying the chemical composition of several species of tea were analyzed and generalized using various chromatographic methods. The review presents a summary of the latest information concerning the chemical composition of a large variety of tea by different chromatographic methods, which has not previously been reviewed. Qualitative and quantitative analyses of volatile compounds, that contribute to flavor and aroma in tea composition were executed by gas chromatography and gas chromatography-mass spectrometry. Low volatility organic compounds were carried out by using high-performance liquid chromatography methods and GC/MS. Determination of catechins and caffeine in different types of tea were investigated by HPLC of the most current published researches. In addition, the materials used in this article can be used in the field of tea research, determination of quality and evaluation of tea components.

References

1. Hicks A. (2008) Current Status and Future Development of Global Tea Production and Tea Products. FAO Committee on Commodity Problems – Intergovernmental Group on Tea, vol. 12, pp. 251-264.
2. Wan, X., Li, D., Zhang, Z. (2008) Green tea and black tea—manufacturing and consumption. Tea and tea products, pp. 1-8.
3.  https://worldoftea.org/tea-chemistry/
4.  http://mateasse.com/index.php?route=pavblog/blog&id=27
5.  Oze I., Keitaro M. (2004) Coffee and green tea consumption is associated with upper aerodigestive tract cancer in Japan. International Journal of Cancer, vol. 135, pp. 391-400.
6.  Chen D. (2004) Green tea and tea polyphenols in cancer prevention. Frontiers in Bioscience, vol.9, p. 2618.
7.  Johnson R., Bryant S. (2012) Green tea and green tea catechin extracts: an overview of the clinical evidence. Maturitas, vol. 73, pp. 280-287.
8.  Harold N. G. (1992) Green tea composition, consumption and polyphenol chemistry. Preventive Medicine, vol.21, pp. 334-350.
9.  Baraboi V. A. Tea plant catechins: structure, activity, application [katekhiny chainogo rasteniia: struktura, aktivnost, primenenie] – 2008. – Vol. 3. – P. 25-36.
10.  Wang H., Helliwell K. (2000) Epimerisation of catechins in green tea infusions. Food Chemistry, vol. 70, pp. 337-344.
11.  Goh R., Jing G. (2015) Green tea catechins reduced the glycaemic potential of bread: an in vitro digestibility study. Food Chemistry, vol. 180, pp. 203-210.
12.  Chen J., Jun X. (2015) Epigallocatechin-3-gallate attenuates lipopolysaccharide-induced mastitis in rats via suppressing MAPK mediated inflammatory responses and oxidative stress. International Immunopharmacology, vol. 26, pp. 147-152.
13.  Wong, M.H., Fung K.F. (2003) Aluminium and fluoride contents of tea, with emphasis on brick tea and their health implications. Toxicology Letters, vol. 137, pp. 111-120.
14.  Pehrsson P., Patterson, Y. (2011) The Fluoride Content Of Select Brewed And Microwave-Brewed Black Teas In The United States. Journal of Food Composition and Analysis, vol. 24, pp. 971-975.
15.  Quock R., James X.G. Tea fluoride concentration and the pediatric patient. Food Chemistry, vol. 130, pp. 615-617.
16.  Koblar A., Tavc’ar G. (2012) Fluoride in teas of different types and forms and the exposure of humans to fluoride with tea and diet. Food Chemistry, vol. 130, pp. 286-290.
17.  http://deeprootsathome.com/tea-brands-pesticides/
18.  https://www.drtaniadempsey.com/single-post/The-Truth-About-Pesticides-in-Tea-Tea-Toxicity-Chemicals-In-Tea
19.  https://dailyhealthpost.com/pesticides-tea/
20.  RMG 19885-74. Tea. Methods for determination of tannin and caffeine content [Chai. Metody opredelenia soderzhaniia tanina i kofeina] Moscow, Russia, 2014
21.  RMG 10727-2013. Tea and instant tea in solid form. Determination of caffeine content. Method using high-performance liquid chromatography [Chaj i bystrorastvorimyj chaj v tverdoj forme. Opredelenie soderzhaniya kofeina. Metod zhidkostnoj xromatografii vysokogo razresheniya] Moscow, Russia, 2014
22.  Silarova P., Ceslova L. (2018) Fast gradient HPLC/MS separation of phenolics in green tea to monitor their degradation. Food Chemistry, vol. 237, pp. 471-480.
23.  Jiao Y, Jiali H. (2017) Nε-(carboxymethyl) lysine and Nε-(carboxyethyl) lysine in tea and the factors affecting their formation. Food Chemistry, vol. 232, pp. 683-688.
24. Shiono T., Yamamoto K. (2017) Selective decaffeination of tea extracts by montmorillonite. Journal of Food Engineering, vol. 200, pp. 13-21.
25. Sökmen M., Demir E. (2018) Optimization of sequential supercritical fluid extraction (SFE) of caffeine and catechins from green tea. The Journal Of Supercritical Fluids, vol. 133, pp. 171-176.
26. Sun H., Qiao F. (2006) Characteristic of theophylline imprinted monolithic column and its application for determination of xanthine terivatives caffeine and theophylline in green tea. Journal of Chromatography A., vol. 1134, pp. 194-200.
27. Rashidinejad A., Birch E.J. (2016) Interactions between milk fat globules and green tea catechins. Food Chemistry, vol. 199, pp. 347-355.
28. Del Rio D., Stewart J.A. (2004) HPLC-MSn analysis of phenolic compounds and purine alkaloids in green and black tea. Journal of Agricultural and Food Chemistry, vol. 52, pp. 2807-2815.
29. Cao Y., Tang H. (2015) A novel method based on MSPD for simultaneous determination of 16 pesticide residues in tea by LC–MS/MS. Journal of Chromatography B., vol. 998, pp 72-79.
30. Engelhardt R. (2013) Determination of amino acids in white, green, black, oolong, pu-erh teas and tea products. Journal of Food Composition and Analysis, vol. 31, pp. 94-100.
31. Baptista J. (1998) Comparison of catechins and aromas among different green teas using HPLC/SPME-GC. Food Research International, vol. 31, pp. 729-736.
32. Xu Y. (2017) Effect of saccharides on sediment formation in green tea concentrate. LWT - Food Science And Technology, vol. 78, pp. 352-360.
33. Du L., Ma L. (2016) Determination of phthalate esters in teas and tea infusions by gas chromatography–mass spectrometry. Food Chemistry, vol. 199, pp. 1200-1206.
34. Zhou Y., Zeng L. (2017) Formation of (E)-nerolidol in tea (Camellia sinensis) leaves exposed to multiple stresses during tea manufacturing. Food Chemistry, vol. 231, pp. 78-86.
35. Ma Ch., Qu Y. (2014) Determination of nerolidol in teas using headspace solid phase microextraction–gas chromatography. Food Chemistry, vol. 152, pp. 285-290.
36. Sasaki T., Koshi E. (2017) Characterisation of odorants in roasted stem tea using gas chromatography–mass spectrometry and gas chromatography-olfactometry analysis. Food Chemistry, vol. 220, pp. 177-183.
37. Kraujalytė V., Pelván E. (2016) Volatile compounds and sensory characteristics of various instant teas produced from black tea. Food Chemistry, vol. 194, pp. 864-872.
38. Han Zh., Rana M. (2017) Data on green tea flavor determinants as affected by cultivars and manufacturing processes. Data In Brief, vol. 10, pp. 492-498.
39. Han Zh., Rana M. (2016) Green tea flavour determinants and their changes over manufacturing processes. Food Chemistry, vol. 212, pp. 739-748.
40. Reto M. (2007) Analysis of vitamin K in green tea leaves and infusions by SPME–GC-FID. Food Chemistry, vol. 100, pp. 405-411.
41. Du L., Li J. (2014) Characterization of volatile compounds of pu-erh tea using solid-phase microextraction and simultaneous distillation–extraction coupled with gas chromatography–mass spectrometry. Food Research International, vol. 57, pp. 61-70.
42. Lin J., Zhang P. (2013) Discrimination of oolong tea (Camellia sinensis) varieties based on feature extraction and selection from aromatic profiles analysed by HS-SPME/GC/MS. Food Chemistry, vol. 141, pp. 259-265.
43. Lv H., Zhong Q. (2012) Aroma characterisation of pu-erh tea using headspace-solid phase microextraction combined with GC/MS and GC–olfactometry. Food Chemistry, vol. 130, pp. 1074-1081.
44. Cho S., Abd El-Aty A.M. (2014) Simultaneous multi-determination and transfer of eight pesticide residues from green tea leaves to infusion using gas chromatography. Food Chemistry, vol. 165, pp. 532-539.
45. Hou X., Lei. Sh. (2016) Optimization of a multi-residue method for 101 pesticides in green tea leaves using gas chromatography-tandem mass spectrometry. Revista Brasileira de Farmacognosia, vol. 26, pp. 401-407.
46. Yang T., Zhu Y. (2016) Enantiomeric analysis of linalool in teas using headspace solid phase microextraction with chiral gas chromatography. Industrial Crops and Products, vol. 83, pp. 17-23.  
47. Venditti E., Bacchetti T. (2010) Hot vs. cold water steeping of different teas: do they affect antioxidant activity? Food Chemistry, vol. 119, pp.1597-1604.
48. Martin-D. (2017) Determination of metalloid, metallic and mineral elements in herbal teas. Risk assessment for the consumers. Journal of Food Composition and Analysis, vol. 60, pp. 81-89.
49. Sharma V. (2008) Influence of milk and sugar on antioxidant potential of black tea. Food Research International, vol. 41, pp. 124-129.
50. Yuksel Z., Avci E. (2010) Characterization of binding interactions between green tea flavanoids
and milk proteins. Food Chemistry, vol. 121, pp. 450-456.

51. Jin C. (2001) Processing procedures of brick tea and Their Influence On Fluorine Content. Food and Chemical Toxicology, vol. 39, pp. 959-962.

52. Zhao H., Yu Ch. (2017) Effects of geographical origin, variety, season and their interactions on minerals in tea for traceability. Journal of Food Composition and Analysis, vol. 63, pp. 15-20.

53. Ye J., Fan F. (2013) Interactions of black and green tea polyphenols with whole milk. Food Research International, vol. 53, pp. 449-455.

54. Jin L. (2016) Antioxidant properties and color parameters of herbal teas in China. Industrial Crops and Products, vol. 87, pp. 198-209.

55. Zen J. (1999) Determination of theophylline in tea and drug formulation using a Nafton®/lead - ruthenium oxide pyrochlore chemically modified electrode. Talanta, vol. 50, pp. 635-640.

56. Marcelo B. L., Andrade S. (2012) Turbidimetric and photometric determination of total tannins in tea using a micro-flow-batch analyzer. Talanta, vol. 88, pp. 717-723.

57. Yin H., Meng X. (2012) Electrochemical determination of theophylline in foodstuff, tea and soft drinks based on urchin-like CdSe microparticles modified glassy carbon electrode. Food Chemistry, vol. 134, pp. 1225-1230.

58. Das S., Letizia M. (2017) Fluoride concentrations in traditional and herbal teas: health risk assessment. Environmental Pollution, vol. 231, pp. 779-784.

59. Cao J. (2004) Safety evaluation on fluoride content in black tea. Food Chemistry, vol. 88, pp. 233-236.

60. Cao J., Zhao Y. (2006) Fluoride levels in various black tea commodities: measurement and safety evaluation. Food and Chemical Toxicology, vol. 44, pp. 1131-1137.

61. Emekli-Alturfan E., Yarat A. (2009) Fluoride levels in various black tea, herbal and fruit infusions consumed in Turkey. Food and Chemical Toxicology, vol. 47, pp. 1495-1498.

62. Jabeen S., Alam S. (2015) Withering timings affect the total free amino acids and mineral contents of tea leaves during black tea manufacturing. Arabian Journal of Chemistry.