DETERMINATION OF IONIC SPECIES IN TEA INFUSIONS BY ION CHROMATOGRAPHY

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The distribution levels of inorganic anions of tea infusions were measured either for monitoring consumers' health issues, or for optimization of manufacturing processes.

A simple, rapid, and accurate method was used for the quantitative determination of fluoride, chloride, nitrate, phosphate, and sulphate ions in green, black, and white tea infusions, by ion chromatography with conductometric detection. The separation was performed using an anion-exchange column at 30^0C by isocratic elution with an aqueous 1.7 mM Na_2CO_3 + 1.8 mM $NaHCO_3$ eluent. Without special sample processing, the method was successfully applied for 24 tea types available in Romanian shops. The ionic content was subjected to multivariate analysis in order to reduce dimensionality and detect the factors responsible for the registered variability.

Keywords: ion chromatography; inorganic anions; conductometric detection; green tea; black tea; white tea

1. Introduction

White, green, oolong, and black teas are produced by the same plant, *Camellia Sinensis*, the differences developing during harvesting and manufacturing. Depending on the manufacturing process, teas are classified into three major groups: non-fermented green tea, semi-fermented oolong tea and fermented black tea [1].

The tea plant leaves are used for preparing the well know social drink and curing different illnesses; since 3000 BC traditional Chinese medicine has recommended green tea for headaches, muscle pain, digestion, detoxification, and for prolonging life. Most of these health benefits are now confirmed. Tea infusion

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is the most commonly consumed beverage worldwide next to water, about 20 billion cups being consumed daily. In Taiwan, the daily average consumption is 2.5 cups of tea infusion per person [2].

The chemical composition of tea is complex, ranging from polyphenols, caffeine, amino acids, carbohydrates, proteins, chlorophyll, volatile organic compounds, to inorganic anions (fluoride, chloride, nitrates, phosphates, sulphates, etc..) heavy metal (e.g. aluminium, copper, cadmium, chromium, etc.) and other unspecified compounds [3]. Organic anions in tea are responsible for the beverage taste and quality, while inorganic and carboxylic acids contribute to the acidity associated with an agreeable aroma and flavour [4]. Fluoride and iodide are very important micronutrients in small concentrations, and become toxic in high concentrations; an incorrect iodide dietary balance can cause thyroid disorders. Excessive fluoride consumption induces symptoms of acute and chronic fluoride toxicity (fluorosis). Liquids are the main source of fluoride intake for humans [5]. The maxim clinically acceptable fluoride content is not well known, but the value of 0.05-0.07 mg F/kg body weight/day is generally accepted as a reference [6].

As for the other ions, their health impact is tremendous. Chloride, the main anion in the extracellular fluid, is responsible for muscle irritability. Phosphorus is essential for tissue growth and renewal. Phosphorus compounds carry, store, and release energy and assist several enzymes and vitamins in extracting energy from nutrients. Nitrates and nitrites induce paralysation of the vasomotor centre, causing vasodilatation of small calibre vessels associated with hypotension and collapse.

Therefore the inorganic ions content should be closely monitored to maintain product quality and to investigate possible violations of patents on competitive products. The literature has reported several analysis methods for leaf tea infusions including high performance liquid chromatography (HPLC), mass spectrometry with inductively coupled plasma (ICP-MS), plasma atomic emission spectrometry inductively coupled (ICP-AES), capillary electrophoresis(CE), etc. and classical methods (photometry, titration, gravimetry). Many classical wet methods suffer from limited sensitivity and interventions. They may require intensive labour and often are difficult to automate.

Several procedures have been proposed for the simultaneous chromatographic separation of organic acids, inorganic anions and cations, and heavy metals in tea infusions. Mixed silica-based ligands containing reversed-phase and ion exchange functions have been proposed for determination of organic and inorganic acids in precipitation samples [4]. Ion chromatography, developed by Small et al [7], allows the simultaneous determination of ions in a short time, displaying good reproducibility of results, high sensitivity [8], small sample volume even for samples with complex matrix [3].

Although many tea samples have been studied and reported in the literature, it is difficult to compare data obtained from different laboratories due to lack of standardized experimental procedures. There are several reports on the determination of mineral anions in tea infusions, as those published by Spiro et al. [9], Buldini et al. [10], Ding et al. [11], Simpson et al. [12], Alcazar et al. [4], Hayacibara et al. [6], Pohl et al. [13], Amin et al. [14]. Michalski [6] has reported an ion chromatographic procedure for the simultaneous determination of several inorganic anions in tea infusions, with the exception of iodide and bromide. In addition, the detection limits reported were rather high. Thus, none of the methods reported to date is suitable for the simultaneous quantitative determination of fluoride, chloride, bromide, iodide, nitrite, nitrate and sulphate in tea infusions [5].

We report in the followings a suppressed ion chromatography method for the simultaneous determination of F^-, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} ions in black, green, and white tea infusions, involving minimum sample processing.

2. Experimental

Ultrapure water, 18.2 MΩ/cm, filtered through a 0.20 μm pore membrane, produced by an Easy Pure Rodi Branstead system was checked for the anion content and used for preparing standard solutions and tea infusions.

A certified F^- 1(00 mg/L), Cl^- (250 mg/L), NO_3^-, SO_4^{2-} (500 mg/L), PO_4^{3-} (1000 mg/L) combined stock standard solution for ion chromatography (Merck), traceable to SRM NIST, was used for calibration purposes. All calibration standard solutions were prepared by diluting the stock appropriately just before use. 0.45 μm pore diameter filters were used for sample particulate removal. All volumetric glassware used was A–class grade.

24 tea samples, purchased from Romanian supermarkets or specialized tea stores, out of which 11 flavoured with jasmine, citric or bergamot were included in the present study. Samples indicatives and main commercial characteristics are collected in table 1. Some were manufacturer packed (17 samples, containing 1.5 or 2 g individual bags, suitable for one cup infusion), others were packed in vendor's own bags (7 samples, weighing 25.00 or 50.00 g).

Infusions were prepared with ultrapure water, adding 2.0 g of tea leaves into 100 mL water at 100 ºC. The covered infusion vessel was left to stand for 10 minutes (infusion time), for complete extraction of inorganic anions. After cooling at room temperature, samples were filtered through a 0.45 μm membrane and further analyzed by ion chromatography and tested for pH and conductivity. Each sample was analyzed twice. Infusions were stored in 100mL sterile plastic containers with tight lids and refrigerated at 4°C, and used for *p*H and conductivity evolution monitoring.

Table 1

Commercial characteristic of studied tea samples

Brand	Manufacturer/ importer	Origin country	Packaging	Tee type	Flavoured / spiced	Indicative
English Breakfast	Althaus	Sri Lanka	bags	black	-	BT6
Grande Ceylon	-	Sri Lanka	bags	black	-	BT2
Lipton Earl Grey	Unilever	India, Sri Lanka	bags	black	bergamot	BT4
Lipton English Breakfast	Unilever	India	bags	black	-	BT3
Lipton Yellow Label	Unilever	Kenya	bags	black	-	BT1
M21- Cafe Creme	Top Tea House	China	batch	black	almond, coconut flakes	BT8
Puerh	Top Tea House	China	batch	black	gingerbread	BT7
China Tea	-	China	batch	green	-	GT1
China Zhu Cha	Althaus	China	bags	green	-	GT12
Grande	Grande	China, Vietnam	bags	green	1.8% lemon	GT4
Green Field – Lotus Breeze	Green Field	China	bags	green	lotus, mint	GT11
Green Field – Tropical Marvel	Green Field	China	bags	green	pineapple, ginger spicy, citrus, apples	GT10
Green Tea	Fares	China	bags	green	lemon, vanilla,	GT17
Jasmine Pearls	Top Tea House	China	batch	green	jasmine	GT13
Lipton	Unilever	China	bags	green	1.5% mandarin, 1.5% orange peel	GT3
Lipton Orient	Unilever	India	bags	green	3.8% oriental spices	GT6
Milford	Milford	-	bags	green	-	GT5
Milk Oolong	Top Tea House	China	batch	green	yes	GT14
Vedda Tea	-	China	batch	green	-	GT2
Vedda Tea	-	China	bags	green	-	GT7
Yamamoto	Top Tea House	Japan	batch	green	yes	GT15
Lipton Asian	Unilever	China	bags	white	-	WT1
White Tea Orange	Top Tea House	-	batch	white	orange	WT2

Ionic content was determined by ion chromatography using an ICS 3000 Dionex ion chromatographic system consisting of an isocratic eluent delivery pump, sample injection port, separation column, suppressor, and conductivity detector. The mobile phase was prepared by diluting with deionised water 1:10 an eluent concentrate (Dionex) containing 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$. All chromatographic experiments were carried out at 30°C. The mobile phase was vacuum degassed before use. The AS4A 4×250 mm analytical column, from Dionex, containing a 15 μm polystyrene/divinylbenzene latex anion exchanger was guarded by an AG4A 4×50 mm guard column. The eluent flow rate was 1.6 mL/min, while the ASRS 300x4 mm suppressor worked at 16 mA.

*p*H and conductance were measured with a Jenaway 3540 pH&conductivity–meter, equipped with a combined pH electrode and a four electrode conductivity cell. pH calibration was carried out using the pH 4, 7, and 10 buffer solutions set provided by the manufacturer, while conductance calibration was carried out with a Consort calibration standard set consisting of 1413 µS/cm (0.01 M KCl) and 12.88 mS/cm (0.1 M KCl) solutions. All measurements were performed at room temperature for five consecutive days.

3. Results and discussion

The experimental separation conditions lead to well–resolved peaks for all five anions of interest in less than 10 minutes, as shown in Fig. 1.

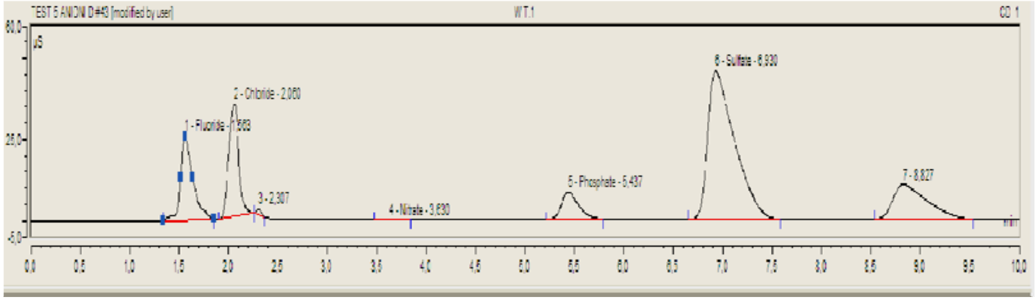


Fig. 1. Typical chromatogram for the WT1 tea infusion sample recorded with the ICS 3000 equipment at 30°C.

Table 2

Calibration curves parameters as obtained by linear regression

Parameter	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Slope	0.2817	0.1866	0.0906	0.0439	0.1173
Slope standard deviation	0.0824	0.0855	0.0434	0.0215	0.0568
Intercept	0.007	-0.00004	-0.0021	-0.0069	-0.0070
Intercept standard deviation	0.136	0.353	0.3582	0.3551	0.4681
Regression coefficient (R^2)	0.9998	0.9999	0.9999	0.9999	0.9999
Residual standard deviation	0.015	0.004	0.009	0.010	0.010
Detection limit, mg/L	0.16	0.07	0.30	0.68	0.26
Quantification limit, mg/L	0.53	0.22	1.00	2.27	0.86

Calibration curves were obtained in the 0.1–30 mg/L concentration range for $F^–$, $Cl^–$, $NO_3^–$, $PO_4^{3–}$, and $SO_4^{2–}$ ions. Experiments ran at six concentration levels, using at least two replicate injections for each anion concentration level. They gave the linear regression parameters in terms of peak area shown in table 2, while a typical calibration curve for phosphate is given in Fig. 2. Limits of detection (LOD) and limit of quantification (LOQ) were calculated as three times and ten times of the residual standard deviation for the regression line and calibration line slope, respectively.

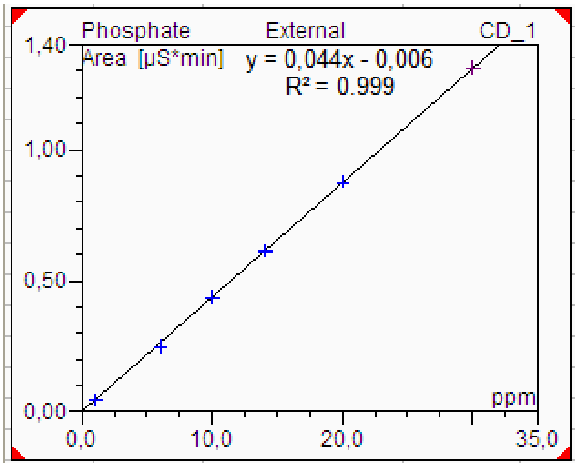


Fig. 2. Calibration curve for phosphate in the 1 – 30 mg/L concentration range

Quantification of anionic amounts present in the set of infusions studied showed large variations for all five anions: fluoride (ranging from 6.36 to 21.23 mg/g, with an average of 13.53 mg/g), chloride (ranging from 3.25 to 10.93 mg/g, with an average of 5.60 mg/g), nitrate (ranging from 0.03 to 2.17 mg/g, with an average of 0.43 mg/g), sulphate (ranging from 6.76 to 61.92 mg/g, with an average of 21.47 mg/g) and phosphate (ranging from 7.26 to 65.89 mg/g, with an average of 21.68 mg/g). They are induced by differences in country of origin, leaves harvesting and processing, including manufacturers' blending policies, addition of fragrances and spices. In terms of maximum allowed levels of anions in foodstuff, there were no overridden values.

There were four types of tea infusions studied, covering the entire processing possibilities: white, green, pu erh, and black. The variations of anion content of different groups of tea infusions are presented in Figs. 3-7. The set of plain green tea infusions is rather homogeneous in terms of fluoride, chloride, nitrate, and phosphate concentrations. There is one odd sample in terms of sulphate concentration, GT12 (34.97 mg/g), originating from China. It seems that it comes from a different region in China than the rest. The nitrate content is particularly small in the entire set, the GT1 sample displaying the highest value, 0.48 mg/g dry product.

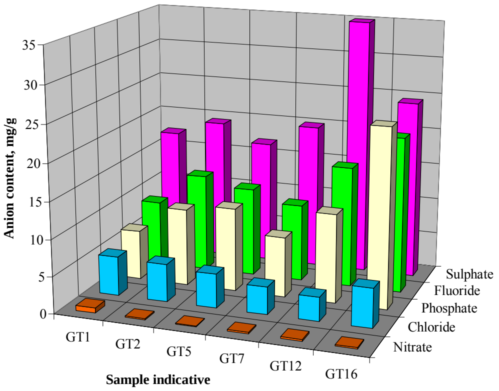


Fig. 3. Anion content in the plain green tea infusions

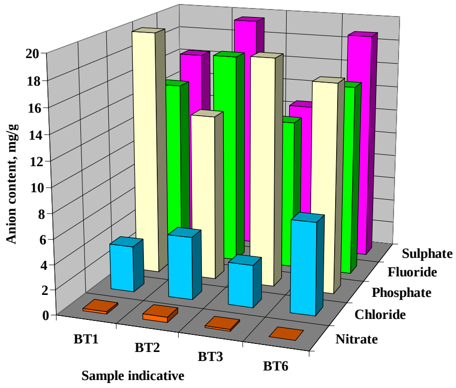
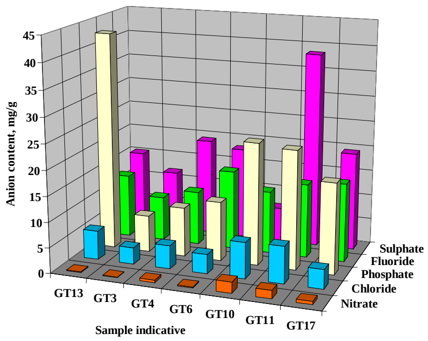


Fig. 4. Anion content in the plain black tea infusions

The plain black tea set presents a higher degree of homogeneity than the green tea set. It seems that processing has levelled the ionic load to a larger extent. There is a higher ionic load for the Sri Lanka teas (BT2, BT6), fact noticed for the chloride, sulphate, phosphate, and fluoride amounts. The pattern is not followed in the case of nitrate, fact connected probably to the use of fertilizers.



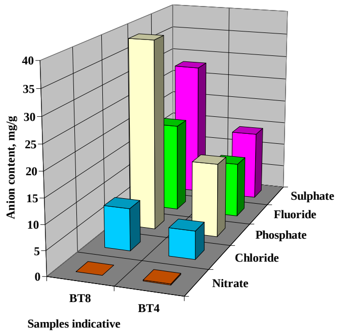


Fig. 5. Anion content in the flavoured green tea infusions

Fig. 6. Anion content in the flavoured black tea infusions

Flavouring with citric, lotus, peppermint, jasmine, oriental spices induces changes in the anions concentration, increasing the ionic load. The nitrate content increases above 0.20 mg/g. There is one exception, the BT8 sample, flavoured with almonds and coconut flakes.

GT11 infusion, flavoured with lotus and peppermint, shows the largest SO_4^{2-} amount, 38.40 mg/g, while GT13 exceeds in terms of PO_4^{3-} content, 42.77 mg/g. The Unilever product from China, GT3, displays the smallest PO_4^{3-}

and Cl^- concentrations in the entire group of studied teas, regardless the origin country and manufacturing procedure.

Two white tea samples, a plain and an orange flavoured one were also analyzed, as well as a pu erh tea infusion. Their anionic content is presented in Fig. 7. The plain white tea sample WT1 is characterized by the largest PO_4^{3-} content (65.89 mg/g) in the entire lot analyzed.

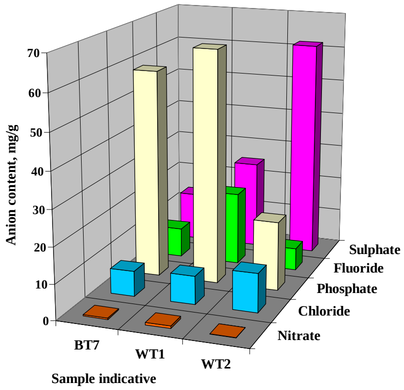


Fig. 7. Anion content of white and black tea infusions.

White tea flavouring does not seem to modify the nitrate and chloride content significantly, but has unexpected effects on the phosphate and sulphate concentrations, lowering the first and increasing the second. This behaviour could be connected to the different origins of the sample and a vendor intervention in the product formula. The orange flavoured white tea WT2 displays an unusually low fluoride concentration, 6.36 mg/g, similar to that characteristic to the plain tea. It is difficult to point out the reason based on the composition of a vendor–packed product (communicating little information about the real composition), but it seems that the orange flavour does not contribute to the fluoride ionic load.

The total anion loads were also compared and it was noticed that they depend on the oxidation degree, decreasing in the order white > green > black. The range spans from 120.25 mg/g plain white tea WT1, to 31.23 mg/g, characteristic to the flavoured Lipton green tea from Unilever, GT3. This behaviour is in line with the degree of leaves processing.

Flavouring increases the total anionic content for all infusions studied. In the Unilever products group, the total anionic load obtained is similar for mixtures originating from India, while the Indonesian product, GT16, has almost twice as much of the studied anions, 75.52 mg/g, rather similar to the other flavoured green infusions included in the study.

India–originating teas distributed by Unilever seem rather homogeneous in terms of total anion content, showing an average of 47.58 mg/g, and similar NO_3^- (0.19 mg/g), Cl^- (4.31 mg/g), PO_4^{3-} (15.05 mg/g), F^- (13.05 mg/g) and SO_4^{2-} (14.98 mg/g) concentrations. As results indicate, it is very likely that the Unilever company uses black or green tea originating from the same Indian region.

The Unilever product from China, GT3, displays the smallest PO_4^{3-} and Cl^- concentrations in the entire group of studied teas, regardless the origin country and manufacturing procedure. India–originating teas distributed by Unilever seem rather homogeneous in terms of total anion content, showing an average of 47.58 mg/g, and similar NO_3^- (0.19 mg/g), Cl^- (4.31 mg/g), PO_4^{3-} (15.05 mg/g), F^- (13.05 mg/g) and SO_4^{2-} (14.98 mg/g) concentrations. As results indicate, it is very likely that Unilever company uses black or green tea originating from the same Indian region.

There is consistency between the fluoride and chloride contents reported in this study for the Lipton tea infusion (12.24 mg/g, 3.42 mg/g respectively) and those reported earlier by Michalski [3] for the same product (12.60 mg/g and 2.01 mg/g).

The anion contents in the present study do not match the black tea contents reported by Alcazar [4] and Spiro [9] groups, or those published by Ding [11] or Spiro [9] for the green tea infusions, due to the different procedures applied for sample preparation and origin of tea leaves.

Conductivity and pH were closely monitored for all infusions included in the study for a 5 days period. The results are collected in table 3.

Initial pH of all infusions studied are in the slightly acidic region, varying in the 4.594 (GT3) and 6.466 (BT1) range, with an average value of 5.384. After a five days period some of the samples displayed variations as high as 0.842 *p*H units, as is the case of the GT3 sample. *p*H variation in time was accompanied by change in colour (when moving to more acidic values) and/or solid phase formation (when moving to more basic values).

Initial conductivity values varied between 526 and 1115 μS/cm, with an 776 μS/cm average value. These variations can be connected to the degree of processing, presence of additives, country of origin, and vendor. After five days variations were recorded, a couple of them being significant enough to be attributed to changes in the total concentration of anions present in the liquid phase rather than to the experimental error.

The plain white tea infusion, WT1, was relatively stable in time as regards *p*H, which was slightly acidic, and conductivity, with a minor tendency to decrease in time. This is correlated to the highest anionic load measured in the present study.

The green tea infusion GT3, having the smallest anionic load showed a tendency of *p*H increase, from 4.594 to 5.436, event also accompanied by a decrease in conductivity from 647 μS to 532 μS. This is the sample that was the quickest in developing a black precipitate.

Table 3

Variation of infusions *p*H and conductivity in a five days time interval

Sample indicative	pH		Λ, μS/cm	
	Day 1	Day 5	Day 1	Day 5
BT1	6.466	6.138	937	784
BT2	4.902	5.479	753	722
BT3	4.759	5.436	674	675
BT4	5.058	5.558	576	547
BT6	4.902	5.004	750	703
BT7	5.216	5.161	903	856
BT8	5.052	5.026	1047	986
GT 10	5.401	5.416	877	829
GT 11	5.655	5.633	888	839
GT 12	5.581	5.563	839	786
GT 13	5.876	5.842	769	731
GT 14	5.535	5.522	532	495
GT 15	4.626	4.64	763	719
GT 16	5.535	5.514	994	933
GT 17	5.378	5.338	715	510
GT1	5.523	6.138	592	625
GT2	5.185	5.479	754	710
GT3	4.594	5.436	647	532
GT4	5.659	5.558	688	656
GT5	6.093	5.519	645	547
GT6	5.533	5.333	679	723
GT7	5.537	5.436	526	510
WT 1	6.052	5.498	961	910
WT 2	5.102	5.087	1115	1073

Multivariate analysis was applied to identify the main source of variability in the anionic content, pH and conductivity measured experimentally in 20 tea samples. The principal component analysis (PCA) was performed considering the standardized data, meaning that initial variables were transformed as to be centered and have unit dispersion. Matab® procedures were applied in PCA. According to PCA, the system dimensionality can be reduced to three principal components, corresponding to eigenvalues of the covariance matrix larger than 1. These components account for 68 % of the variability of the studied lot: PC1 accounts for 30.86 %, PC2 for 20 % and PC3 for 17.18 %, as shown in Fig. 8. The variables with higher discrimination power according to the statistical procedure were Cl^- (0.6225 loading in PC1), NO_3^- (0.5178 loading in PC2), PO_4^{3-} and SO_4^{2-} (approximately equal loadings in PC1 and PC2). F^- species has a small participation in PC1 and PC2, while its contribution in PC3 raises above 0.7.

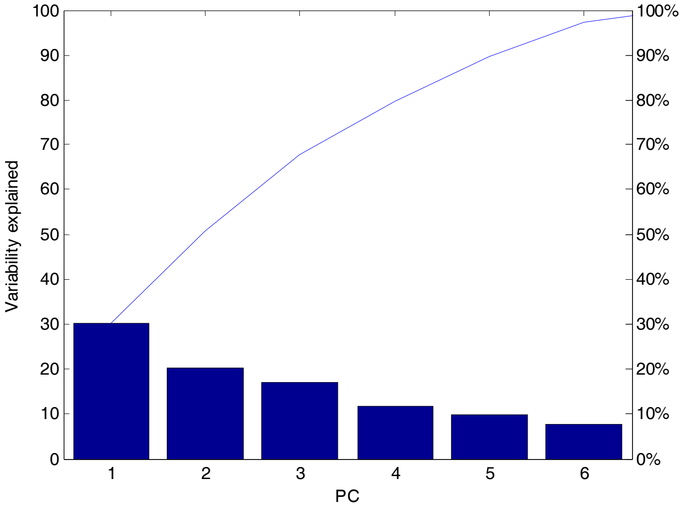


Fig. 8. Contribution of the principal components to the explained variability of the analyzed data

Fig. 9 shows the loadings corresponding to each parameter in the first 2 PCs, as well as the relative sign in the correlation relations that define the PCs as a linear combination of the variable investigated in the studied lot. It can be concluded that Cl^- is the ionic species that induces the most important variability.

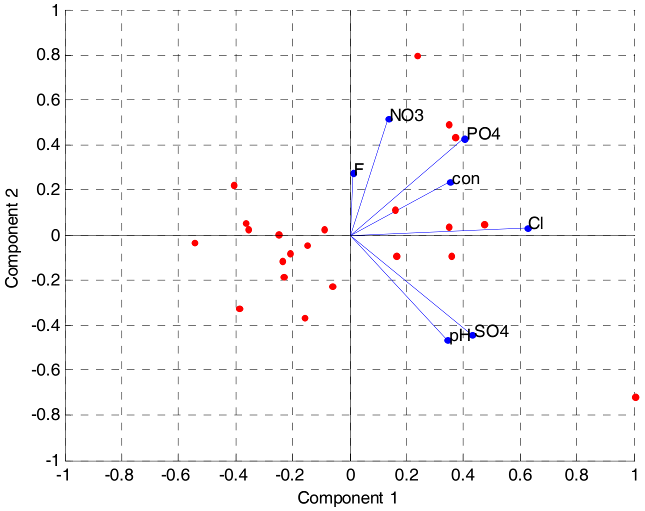


Fig. 9. Biplot of investigated tea lot

The graphical representation of the samples in PC1-PC2 coordinates doesn't reveal a fairly good separation between green, black, and white tea in fusions (Fig. 10).

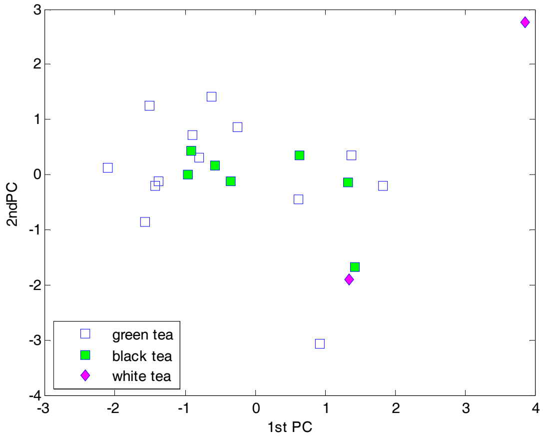


Fig. 10. Sample plots for PCA

Discrimination of tea types according to the fluoride, chloride, nitrate, phosphate, and sulphate ions content, together with pH and conductivity was not possible, suggesting that other characteristics of the tea infusions should be taken into consideration when performing the multivariate analyses.

6. Conclusions

A simple ion chromatographic method was proposed for the simultaneous quantification of five inorganic anions: chloride, fluoride, nitrate, sulphate and phosphate. Isocratic elution with carbonate/sodium bicarbonate (1.8 mM/1.7 mM) and conductometric detection enabled efficient separation of all five ions within 10 minutes. The simplicity of sample treatment recommends the procedure for routine analysis of inorganic anions in tea infusions.

Anions contents varied in large limits, showing dependence on the harvesting and processing undergone by the tea leaves, country of origin, and degree of aromatization. The highest ionic load was found in white tea infusions, and it decreased while moving to green and black types. Experiments demonstrated that flavouring affects significantly the anionic content, a general increasing trend being noticed. The exceptions identified could be related to the geographical origin or vendors special mixing procedures. Black tea infusions displayed the highest variation in ionic content, fact shown by the chromatographic investigations, as well as in the pH and conductivity monitoring over time. The variability of the entire data set can be attributed to the Cl^- and NO_3^- content. The characteristics evaluated so far do not allow discrimination of tea types, and attention should be oriented to the presence of other species before attempting advanced classifications.

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