MULTIELEMENTAL ANALYSIS OF TEAS, HERBS AND THEIR INFUSIONS BY MEANS OF TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROSCOPY

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Abstract − In this work, total reflection X-ray fluorescence (TXRF) spectroscopy was used for the simultaneous multi-elemental determination of thirteen elements (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba and Pb) in 38 tea and herb samples. Infusions were also prepared and analysed by TXRF in order to determine the solubility of each element. Principal component analysis (PCA) was applied by using the elemental concentration values for the differentiation purposes.

Keywords: tea, herbs, infusions, TXRF, principal component analysis

1. INTRODUCTION

Tea, an evergreen plant belonging to the family of the Camellia sinensis, is one of the most popular non-alcoholic beverages world-wide, due to its aroma, taste, smell, variety of types and multiple positive health-promoting effects [1-4]. The best known varieties of tea are: white yellow, green, oolong, black and pu-erh. Among them, green, oolong and black are the most popular and differ only from the degree of fermentation of leaves [5].

Tea leaves besides organic compounds such as flavonoids, amino-acids, proteins, enzymes, vitamins, aroma-forming substances, volatile oils and carbohydrates contains as well a high content of major, minor and trace elements [5].

Numerous studies have shown that tea infusion consumption contributes to the dietary intake of some elements such as Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Se, V and Zn. Moreover, tea infusion consumption is linked with anti-oxidant activity, protective effect against cancer, vascular diseases, hypertension, dental caries and reduction of blood cholesterol levels [6-9]. However, some potentially toxic elements such as As, Cd, H and Pb, can be present in tea due to growth environment pollution and thus putting the human health in risk [9]. For this reason, the knowledge of both essential and toxic element content in tea, herbs and their infusions, is of great importance and interest for tea consumers and producers.

Usually, elemental analysis of teas and herb infusions is performed by inductively coupled plasma mass or atomic emission spectrometry (ICP-MS and ICP-AES) [10, 11].

Total reflection X-ray fluorescence spectrometry is another technique that during the last years has achieved interest for elemental composition analysis of foodstuff [12]. TXRF is a variation of energy dispersive X-ray fluorescence spectrometry that has a higher sensitivity and detection limits in the ppb level. TXRF has several advantages such as low amount of sample used for analysis (few µL or ng) and faster and simpler qualitative and quantitative analysis. The introduction of new low power benchtop TXRF systems which are really cost-effective and do not require gas or cooling media for operation has increased the spread of TXRF use. So far, only two contributions related with analysis of tea and herb infusions by means of TXRF are reported in literature. In these two works, large-scale TXRF instrumentations with high-power X-ray tubes were employed [13, 14].

In the present study, TXRF was used to determine the elemental content of solid tea and herb samples and the elemental solubility into infusion. Twenty-eight tea samples (black, green and oolong) and 10 different herbs and their infusions were analysed. For botanical differentiation of tea and herb samples, PCA was also applied by using elemental concentration values.

2. EXPERIMENTAL

A set of seventeen black (B1-B17), ten green (G1-G10) and one oolong tea (O1), one ginseng (E1) and nine mixed herbs (I1-I9) were investigated in this study. All the samples from different brands and different provenance are commercial.

About 250 mg of solid sample was added in quartz vessels with 9 mL of nitric acid and 1 mL of hydrogen peroxide and digested with a microwave digester (Discover SP-D Explorer, CEM Corporation). The digestion program consisted in 6 min at a temperature of 200 °C, a power of 300 W and pressure of 300 psi. After cooling, digested sample solutions were transferred to a 50 mL flask and brought to volume with ultrapure de-ionized water. From each sample digest, an aliquot of 1 mL was fortified with a suitable volume of a Ga solution used as internal standard to have a final concentration of 1 mg/L.

For the preparation of infusions, it was maintained the same ratio (sample-mass to water-volume). Firstly, 50 mL of ultrapure de-ionized water was added in a glass beaker and brought to boil in a hot plate. Then it was added about 250 mg of the sample and a magnetic stirrer was added for agitation so as to improve the extraction of organic and inorganic matter. The extraction time under agitation was 5 min. Subsequently, the infusion was left to decant for 10 min and then a proper volume of solution was taken in order to add the internal standard (Ga=1mg/L) for quantification.

Triplicates were prepared for each sample and 10 µL were deposited on a siliconized quartz reflector and dried by a hot plate. TXRF characteristics of Bruker S2 Picofox equipped with a Mo tube are displayed in Table 1.

Table 1. Instrumental setup and measurement conditions of TXRF spectrometer.

TXRF characteristics	
X-ray tube	Air-cooled metal ceramic
Power	40 W
Optics	Multilayer monochromator (17.5 keV)
Detector	Silicon drift detector, Area: 30 mm², FWHM: 139.43 eV (Mn Kα)
Atmosphere	Air
Voltage	50 kV
Current	750 µA
Measuring time	600 s

3. RESULTS AND DISCUSSION

3.1. Total elemental content

Potassium, Ca, Mn and Fe are considered as the major constituents of tea samples with levels of mg/g or higher. In fact, K content levels ranged from 7300 to 15400 mg/kg in both, made teas and mix herb samples. Lower concentration (4300 mg/kg) was found in the ginseng herb sample. Contrarily, Ca concentrations were similar in made teas and ginseng herb sample (2000-7100 mg/kg), while much higher values are determined in the mix herb samples (4400-13300 mg/kg).

As already reported [5] made teas are a rich source of Mn. Our studied tea samples showed a high content of Mn (162-1150 mg/kg) compared to the herb samples (6-278 mg/kg). The content of Fe was similar in made teas (63-1140 mg/kg), as well as in herb samples (80-1670 mg/kg). Titanium, Cu, Zn, Rb, Sr and Ba are minor elements with concentrations in the range 10-450 mg/kg. The highest Zn concentrations were measured in black teas, while values were comparable in green and oolong tea and herb samples. For Ti, Sr and Ba, the highest levels were measured in mix herb samples. The concentration of trace elements (Cr, Ni and Pb) was similar in made teas and herb samples (<13 mg/kg).

3.2. Elemental extraction efficiencies

The percent of elements in infusions (extraction efficiency) was estimated as the ratio of their concentration in infusion to total concentration. In agreement with literature reported data [5] K, Ni and Rb were the highest extractable elements into infusions of tea and herb samples with a solubility in the range of 36 to 100 %. Calcium is considered a poorly extractable element in tea infusions (<20%) and in fact similar values (11 – 26%) were found for our studied tea samples. The extraction of Ca was significantly higher in herb samples (35 – 66%).

Chromium was detected only in the infusions of black tea with a solubility of ≤40%. Manganese in tea infusions was extracted moderately with a range of 25 – 52%. Higher solubility (27 – 91%) was determined in the infusions of herb samples. Iron and Sr are poorly extractable elements and a solubility of 1 to 34% and 4 to 17% were found in tea infusions, respectively. For the infusions of herb samples, these elements showed a higher solubility

(Fe: 4 – 48%, Sr: 30 – 71%). The extraction of Cu into infusions of made teas and mix herb samples was in the range of 4 – 78%, while the ginseng sample presented a higher solubility (90%). The solubility of Zn in all samples ranged between 7 and 100% in agreement with ranges reported in literature. Barium was extracted poorly in tea infusions (≤21%), while a solubility up to 76% was found in herb infusions. Lead was detected in just one herbal sample. The pie charts in Figure 1 show the preferential extraction of each element in tea and herb samples.
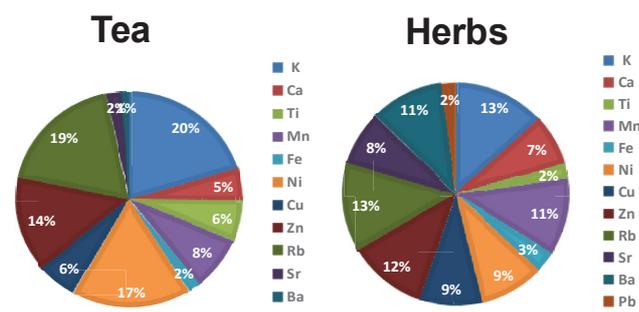

Fig. 1. Preferential extraction (%) of elements determined in tea and herb samples.

3.2. Principal component analysis

The content of all elements determined in tea, herbs and their infusions have been used to apply PCA for differentiation of two groups of samples: teas and herbs (Figure 2).
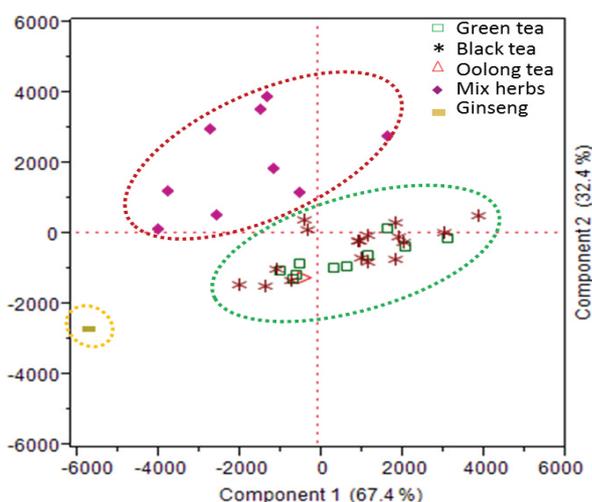

Fig. 2. Scatter plot using concentrations of all elements determined in infusions of tea and herb samples.

PCA was performed using covariance matrix on the complete raw data set (concentration values). The scatter plot of 28 teas and 10 herb samples show a projection of the first two principal components representing 99.8% of the total variance (component 1 = 67.4%, component 2 = 32.4%). As we can see, a clear differentiation between tea, herbs and ginseng samples is obtained.

4. CONCLUSIONS

In this work, TXRF was applied for elemental analysis of tea, herb samples and their infusions. The analytical results reported in this study on the concentrations of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba and Pb in 38 samples of different kinds of tea and herbs, as well as on their solubilities into infusions, could be useful when assessing the intake of these elements by tea/herb infusion drinking. Moreover, the elemental composition together with principal component analysis allowed identifying the group of tea and herb samples and thus helping quality control analysis.

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