Microchemical Journal 98 (2011) 186–189

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Polarized X ray fluorescence spectrometer (EDPXRF) for the determination of essential and non essential elements in tea

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ARTICLE INFO

Article history:
Received 11 January 2011
Accepted 20 January 2011
Available online 2 February 2011

Keywords:
EDPXRF
Essential elements
Toxic elements
Tea

ABSTRACT

Polarized X ray fluorescence spectrometer (EDPXRF) is employed for the determination of essential and non essential elements in several kinds of tea marked in Italy. The quality of data was assured by calibrating the instrument with certified reference materials. The elements are found to be present in the different kinds of tea in various proportions depending on soil composition and the climate in which the plant grows.

1. Introduction

Tea is one of the most widely popular nonalcoholic beverage: after water, it is the most widely consumed beverage in the world [1]. Tea is the agricultural product of the leaves, leaf buds, and internodes of the *Camellia sinensis* plant, prepared and cured by various methods. "Tea" also refers to the aromatic beverage prepared from the cured leaves by combination with hot or boiling water, and is the common name for the *C. sinensis* plant itself. It has a cooling, slightly bitter, astringent flavor which many enjoy. There are at least six varieties of tea: white, yellow, green, oolong, black, and pu-erh. The three most popular types of tea (green, oolong, and black) are distinguished on the basis of degree of fermentation. The leaves of green tea are dried and roasted but not fermented, whereas black tea leaves are additionally fermented. If the leaves are only partially fermented, then oolong tea is the result. After fermentation, tea is rated with respect to aroma, color, and taste.

Humanity uses the tea infusions from ancient times as a delectable item or as a natural medicine since the tea bush is known to accumulate trace metals. The hot water extracts a part of the elements incorporated and by drinking the infusions they are introduced in human organisms, including the most toxic ones. Many studies have concluded that the consumption of the beverage obtained from infusion of tea leaves has numerous beneficial effects on health, including the prevention of many diseases such as cancer, Parkinson's disease, myocardial infarction, and coronary artery disease [2]. Tea could be an important source of manganese and the large amount of potassium in it could be beneficial for hypertensive patients [3]. However, some undesirable trace elements, such as arsenic, chromium, cadmium, lead, etc. are a concern of this beverage's consumers. Chronic exposure to high levels of inorganic As in drinking water has been found to result in a variety of adverse health effects, including skin and internal cancers and cardiovascular and neurological effects. Long-term exposure to Pb may lead to memory deterioration, prolonged reaction times and reduced ability to understand. MeHg is highly neurotoxic and its adverse effects can be expressed in multiple organ systems throughout the lifespan. Cd exposure may pose adverse health effects, including kidney damage and possibly also bone effects and fractures. Al is thought to be associated with Alzheimer's disease [4]. The tea plant, *C. sinensis*, is one of the few plants that accumulate Al, making tea a major source of dietary Al; aluminum in tea leaves have been reported to reach 23,000 ppm levels which is considered higher than other plants that do not normally exceed 200 ppm [5].

Plants obtain these trace elements from growth media, nutrients agro inputs and soils. Tea soils are acidic and this condition favors solubility of heavy metals. Tea bushes adjacent to heavy traffic gets exposure to Pb and Cd through fallout from automobile exhaust and dust. Other sources include pesticides and fertilizers.

Determination of elemental composition, particularly of heavy metals in tea samples is important from two aspects: to judge their nutritional value and to guard against any probable ill-effect, they may cause to human health. A lot of researches have been done to check the presence of undesirable trace elements in air, water, sediments, soil, animal and human beings, but comparatively less work has been done on the presence of these elements in tea due to

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doi:10.1016/j.microc.2011.01.008

the analytical difficulties associated with both the separation of such components and their quantitative measurements. Elemental composition of tea leaves is normally different according to the type of tea (green or black) and geological source [6]. This study aimed to evaluate the content Mn, Fe, Co, Cu, Zn, Ni, Cr, Cl, Br, I, K, Mg, Ca, P, S, Al, Rb, Sr, As, Cd, Sn, Pb and Hg in several kinds of tea marked in Italy by polarized X ray fluorescence spectrometer (EDPXRF).

EDPXRF is a simultaneous, reliable, sensitive, quantitative multi-elemental and non-destructive technique, suitable for routine analysis due to minimal sample preparation. This technique has been used successfully by various authors for the characterization of different complex matrices.

The elements taken into account are 23 subdivided in essential (macro and micro) and nonessential or toxic. An element is considered essential if the plant fails to grow normally and to complete its life cycle, if grown in a medium adequately removed from the element, whereas in the presence of the suitable chosen concentration of the element it grows and reproduces normally [7].

Among the essential elements estimated in the present work we found the micro and trace elements (Mn, Fe, Co, Cu, Zn, Ni, Cr, Cl, Br, I) and macro elements (K, Mg, Ca, P, S); along the nonessential elements and the toxic elements Al, Rb, Sr, As, Cd, Sn, Pb and Hg are taken into account.

Essential metals can also produce toxic effects when the metal intake is in high concentrations [8]; whereas nonessential metals are toxic even in very low concentrations for human health and environment [9].

Potassium and magnesium are essential electrolytes for maintaining normal fluid balance in cells and a delicate balance of these two elements is reported to prevent an increase in blood pressure and to maintain normal cardiac rhythm. Calcium is known to be involved in muscle contraction and relaxation, blood clotting, proper nerve function and body immune defenses. The biological roles of K, Mg and Ca are essential for disease prevention and control.

Chloride is the chief anion of extracellular fluid which is responsible for muscular irritability. P is essential for growth and renewal of tissues. Phosphorus compounds carry, store and release energy and they assist many enzymes and vitamins in extracting the energy from nutrients.

Fe, Cu, Mn and Zn are essential elements in the enzyme metabolism. They have immunomodulatory functions and thus influence the susceptibility to the course and the outcome of a variety of viral infections [10]. The importance of iron in maintaining good health and well being has long been recognized by nutritionists. Manganese plays a vital role in the control of diabetes, while Zn acts as antioxidant, reducing oxidative damage to cellular DNAs, while enhancing the function of the immune system [11]. Co in the form of Vitamin B-12 is in its physiologically active form. Its deficiency causes impairment of the central nervous system, impairment of neurotransmission, and decline of the immune function [12].

Although there are no reported physiological effects of Sr and Rb at low concentrations, their accumulation in the body system could be detrimental to health. Cd, Pb, Hg and Al have no known physiological function yet reported. They are reported to be toxic and should be considered as a high risk factor to public health in general [7].

2. Experimental

2.1. Samples and sampling

18 kinds of trade label of tea (around 100 g each kind) were purchased from the local Italian markets in April 2010 in the dried leaves form which are the most common part suitable for the preparation of an infusion. The samples analyzed are given in Table 1.

Table 1
Tea samples selected in this study and their composition.

Samples	Composition
Tea 1	Mix of classic Java green tea
Tea 2	Chinese green tea + aroma of jasmine
Tea 3	Sri Lanka black tea + aroma of lemon
Tea 4	Mix of classic Java green tea
Tea 5	Mix of green tea, decaffeinated
Tea 6	Black tea, decaffeinated
Tea 7	Mix tea, decaffeinated
Tea 8	Chinese black tea + aroma of bergamot
Tea 9	Green tea
Tea 10	Mix tea, decaffeinated
Tea 11	Sri Lanka green tea
Tea 12	Sri Lanka black tea
Tea 13	Green tea, decaffeinated
Tea 14	India, Sri Lanka, Kenya black tea
Tea 15	Mix tea
Tea 16	Decaffeinated tea
Tea 17	Black tea
Tea 18	Black tea

2.2. Analytical methods

Samples were dried in an oven at 80 °C until constant mass was obtained. The dry mass value was used to determine the concentration. Then the samples were measured by polarized X ray fluorescence spectrometer.

Each sample was prepared by finally pulverizing the dried materials in a vibrating mill (equipped with a zirconia made grinding system) and mixing it with the paraffin wax Wachs-C 80004005 Mikropulver; finally, the sample was reduced to tablet under pressure.

The determinations were done with a Spectro-X-LAB2000 (SN DK 949196), energy dispersive, polarized X ray fluorescence spectrometer (EDPXRF).

The quality of data was assured by calibrating the instrument with the following certified reference materials (CRM): MURST-ISS-A1 Marine sediment, GBW07310 Stream sediment, GBW07310 Stream sediment, GBW08303 Farmland Soil, LGC6138 Soil, SRM 12-3-12 Sludge, STD 12-1-12 Fly ash, BCR CRM 144R Sludge, CCRM LKSD1 Lake sediment, CCRM PACS-2 Marine sediment, NIST SRM 2709 Agricultural soil, NIST SRM 2711 Montana soil, NIST SRM 1633b Fly ash. The analytical precision, measured as relative standard deviation, for Pb, Cd, As, Zn, Cu, Ni, Mn and Cr, was routinely between 10 and 6%, but about 10% for Cr. The average analytical standard errors observed with the reported certified materials were below 10% for Cr, As and Cd, and below 7% for Mn, Ni, Cu, Zn and Pb.

3. Results and discussion

Tables 2–5 show the concentration of K, Rb, Mg, Ca, Sr, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, Hg, Pb, P, As, S, Cl, Br, and I for the tea samples analyzed; the arithmetical mean and standard deviation were calculated for all elements too. For the element concentrations below the detection limit, MDA was considered. An examination of the data from Tables 2–5 shows that the different kinds of tea contain the elements in various proportions.

Along macro elements, K ranges from 11,717 to 16,514 mg kg^{-1}_{dry} (max concentration for tea 6, black tea, decaffeinated); Mg from 203 to 1322 mg kg^{-1}_{dry} (max concentration for tea 6, black tea, decaffeinated); Ca from 2804 to 5167 mg kg^{-1}_{dry} (max concentration for tea 6, black tea, decaffeinated); P ranges from 883 to 1602 mg kg^{-1}_{dry} (max concentration for tea 5, mix of green tea, decaffeinated). Cl ranges from 324 to 645 (max concentration for tea 6, black tea, decaffeinated).

As it was expected, K exhibits uniform distribution in the samples of different origin; this fact is the consequence of the role K^+ played in the plant metabolism, as a cell osmotic pressure regulator. As with