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Analytical Methods

Speciation of chromium and its distribution in tea leaves and tea infusion using titanium dioxide nanotubes packed microcolumn coupled with inductively coupled plasma mass spectrometry

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Titanium dioxide nanotubes (TDNTs) were used as a solid phase extraction adsorbent for chromium species by a packed microcolumn coupled with inductively coupled plasma mass spectrometry (ICP-MS), including total, suspended and soluble chromium as well as Cr(III) and Cr(VI) in tea leaves and tea infusion. The experimental results indicated that Cr(III) was quantitatively retained on TDNTs in the pH range of 5.0–8.0, while Cr(VI) remained in the solution. The total chromium was determined after reducing Cr(VI) to Cr(III). The concentration of Cr(VI) is calculated by the difference between total chromium and Cr(III). Under optimal conditions, the detection limits of this method were 0.0075 ng mL^{-1} for Cr(III). The relative standard deviation was 3.8% ($n = 9$, $c = 1.0$ ng mL^{-1}). This method was applied for the analysis of the speciation of chromium and its distribution and content in tea leaves, tea infusion and a certified reference material of tea leaves with satisfactory results.

1. Introduction

It is well known that tea, as an agricultural product of the leaves, leaf buds and internodes of the plant (*Camellia sinensis*), has become one of the most widely popular nonalcoholic beverages, consumed by over two-thirds of the world's population due to its medicinal, refreshing and mild stimulant effects (Balentine, Wiseman, & Bouwens, 1997; Karak & Bhagat, 2010). Tea can be cultivated in many regions that have a high humidity, fair temperature and acidic soils, from sea level to high mountains (Hara, Luo, Wickremashinghe, & Yamanishi, 1995). A study has demonstrated that the presence of trace elements (metal with a high relative atomic mass) in tea is due to tea plants being normally grown in highly acidic soils, where trace elements are potentially more bioavailable for root uptake (Han, Zhao, Shi, Ma, & Ruan, 2006). Based on their respective manufacturing techniques, mainly four types of tea, including black or red, oolong, green and white tea, are generally used for tea infusion (water extract from fermented tea leaf) worldwide. In tea infusion, there are many microelements, which may have beneficial or adverse effects on human health. Owing to its beneficial or toxic effect on human health, the speciation of an element, its distribution and content are drawing more and more attention in the fields of toxicological, nutritional and food sciences (Comez & Callao, 2006; Pazos-Capeáns et al., 2006).

Chromium is a ubiquitous element in the environment, originating from natural sources and human activities. Due to its natural and anthropogenic occurrence, chromium is inevitably discharged into the environment. Furthermore, it may enter the food chain from environmental media such as water, soil and air, and then invade the human body. In particular, chromium is of great interest because its toxicity highly depends upon its chemical forms and concentration. Cr(III) is considered to be essential to mammals for the maintenance of glucose, protein and lipid metabolism, whereas Cr(VI) is detrimental to human health even at relatively low concentration levels because it may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers (El-Shahawi, Hassan, Othman, & El-Sonbati, 2008). Therefore, knowledge of the speciation of chromium in agricultural products is of great importance in food production, nutrition and safety. Up to date, however, the information on the speciation of chromium and its distribution in tea leaves and tea infusion has not drawn enough attention in the literatures, including total, suspended and soluble chromium as well as Cr(III) and Cr(VI).

In general, elemental speciation can be carried out by combining an effective separation method with a sensitive detection technique. Of many detection techniques available, inductively coupled plasma mass spectrometry (ICP-MS) has received increasing attention due to its excellent analytical performances such as high sen-

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sitivity, wide linear range and multielement measurement capability. Unfortunately, however, the direct application of ICP-MS for the determination of trace elements in a real sample can only yield information on its total concentration. In order to obtain information about its chemical form, an effective separation and preconcentration technique for different species is usually required before analysis. A variety of methods, including solvent extraction, solid-phase extraction, cloud point extraction, chromatography and catalytic cathodic stripping voltammetry, have been developed for elemental speciation (Narayana, Reddy, Subbarao, Inseong, & Reddy, 2010; Narin, Kars, & Soylak, 2008; Nehir, Mervegül, Sezgin, Ataman, & Mürvet, 2011; Richard et al., 2006; Shahryar & Atousa, 2012). Among them, solid-phase extraction (SPE) has attracted considerable interest in the separation and preconcentration of substances because of its major advantages, including convenience, time saving, low cost, reduced solvent utilisation, high concentration factor, possible miniaturisation and easy automation. It is worth noting that adsorbent material plays a fundamentally crucial role in the SPE technique for selective separation and preconcentration of different species (Lemos et al., 2008; Li, Yang, & Jiang, 2012). In recent years, nanometer-sized substance has drawn growing attention in analytical sciences owing to its small size, large specific surface area, excellent mechanical strength, high chemical stability and unique electrical property. Different nanometer-sized materials have been successfully used as adsorbents for the preconcentration and separation of metal, nonmetal ions and their speciation in various samples (Chen, Xiao, Lu, Hu, & Zhan, 2007; Cui et al., 2006; Tuzen, Saygi, & Soylak, 2008; Yiwei, Yinyan, Deyan, Fang, & Junxia, 2007). In our previous work, single-wall carbon nanotubes were used for the separation and preconcentration of Cr(III) and Cr(VI) in water samples with a simple matrix (Chen, Zhu, Lu, Cheng, & Zhou, 2010).

Titanium dioxide nanotubes (TDNTs), as an interesting member of nanomaterials, have been used for photocatalysis and dye-sensitised solar cells. It was proved that they have a larger surface area than titanium dioxide nanoparticles and carbon nanotubes reported largely in the literatures (Tsai & Teng, 2004). In addition, they provide very attractive features such as durability, corrosion-resistance, non-toxicity and low cost. These facts reveal that TDNTs may be a promising adsorbent for the preconcentration and separation of different substances. To the best of our knowledge, however, study on the use of TDNTs for chromium speciation has received little attention so far.

In this work, we reported an on-line microcolumn packed with TDNTs coupled to ICP-MS for speciation and quantification of chromium, including total, suspended and soluble chromium as well as Cr(III) and Cr(VI) in tea leaves and tea infusion. The adsorption behaviours of analytes on TDNTs were investigated systematically. Experimental parameters affecting the separation and determination of analytes were optimised in detail. Accuracy and feasibility were validated by the analysis of real samples and a certified reference material. Although the number of samples is limited in this work, the present study may provide a potential technique for the speciation of chromium and its distribution in different food, biological and agricultural products with a complex matrix.

2. Materials and methods

2.1. Chemicals

The stock standard solution of chromium (1.0 mg mL^{-1})was obtained from the National Analysis Center of Iron & Steel (Beijing, China); Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Tianjin Reagent Factory, Tianjin, China) in 0.1 mol L^{-1} HNO_3. Working solutions were prepared daily by appropriate dilution of stock solutions. All reagents used were ultrapure or at least of analytical grade. High purity deionised water was used throughout this work. All glassware and containers were soaked in acid solution for at least a day and rinsed thoroughly with ultrapure water before use.

TDNTs were synthesised with the hydrothermal method according to the literature (Wang, Tao, Weng, Song, & Tao, 2004) and characterised by the linear portion of BET plots and scanning electron microscope (Japan). The specific surface area and medial aperture of TDNTs were 348 m^2/g and 4.53 nm, respectively.

2.2. Apparatus

The instruments and determination parameters in this work were described in our previous work (Chen et al., 2010) except nebulizer argon flow rate (0.95 mL min^{-1}).

2.3. Column preparation

Sixty milligrams of TDNTs were introduced into a PTFE microcolumn by the method described in the literature (Chen et al., 2010). Before use, the microcolumn was successively washed with 1.5 mol L^{-1} HNO_3 solution and high purity deionised water until no blank signal was detected by ICP-MS. Then, the column was conditioned to the desired pH value with HNO_3 and CH_3COONa solution for the preconcentration and separation of analytes.

2.4. Sample pretreatment

For the determination of total chromium, an accurately weighed sample portion of 0.1000 g was mixed with 4.0 mL of HNO_3 (65–68%, w/w) and 2.0 mL of H_2O_2 (30%, w/w) in a Teflon pressure vessel. The vessel was closed and left to stand overnight. The digestion vessel was then placed into a microwave oven. After that, the sample was digested in a microwave oven at 180 °C for 15 min. After cooling, the obtained solution was heated to near dryness. The residue was dissolved with 0.1 mol L^{-1} HNO_3 solution, and then diluted to a desired volume with ultrapure water. Procedural blank was exactly prepared in the same way.

Tea infusion was prepared by a conventional method (generally, infuse tea three times). 2.000 g of green tea sample (obtained from Enshi, Hubei, China) was weighed, and placed into a 100 mL glass beaker with 20 mL of deionised water. The beaker was placed on a hot plate, and then water and sampled tea were boiled for 5 min. After cooling, the solutions were transferred into a polypropylene beaker. The residue was re-leached two times, following the former procedure. The three combined extracts were mixed for future use.

To obtain the concentrations of suspended and soluble chromium, a desired volume of tea infusion was taken, and then filtered through a 0.45 μm membrane filter. The insoluble residues attached to the membrane were carefully rinsed down with deionised water. The residues and filtrate were digested by the method mentioned above for the determination of total amount of suspended and soluble chromium in tea infusion, respectively. In addition, the filtrate was also applied for direct analysis of Cr(III) and Cr(VI) without digestion. The same procedure was used for the preparation of blank solution.

2.5. General procedure

A portion of sample solution containing chromium species was prepared, and the pH was adjusted to the desired value with HNO_3 and CH_3COONa before the determination. The obtained solution was passed through a column with a peristaltic pump. Cr(III) was retained on the column, while Cr(VI) remained in the effluent. Afterwards, the sorbed Cr(III) was eluted with 2.0 mL of 1.5 mol L^{-1}