



A green microextraction method in a narrow glass column for copper in artificial saliva extract of smokeless tobacco products



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ABSTRACT

A green non-dispersive ionic liquid based microextraction (ND-IL μ E) method was proposed for the preconcentration of trace levels of copper (Cu²⁺) in artificial saliva extract (ASE) of smokeless tobacco products (SLT). A 100 cm long, narrow glass column containing aqueous solution of Cu/ASE was used to increase phase transfer ratio by providing more contact area between two medium, which drastically improve the recovery of Cu-PAN complex into ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [C₄mim][PF₆]. At optimum experimental conditions, the detection limit and the enhancement factor were found to be 0.042 μ g L⁻¹ and 85, respectively. This method was successfully applied to real samples.

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Introduction

The consumption of different SLT products is very common in South Asia. These products can be used orally or nasally. Now a day the interest is growing in the patterns, distribution, consumption, and compositions of SLT products and their use in various parts of the world [1,2]. Chewing tobacco products contain heterogeneous ingredients including dry tobacco leaves, slaked lime, areca nut, spices, flavors and sweeteners [2]. It was reported that tobacco and areca nut have carcinogenic effects [3] and physiological disorders amongst users [4]. Other data suggest that there is also a risk of negative reproductive outcomes for female users [5].

Gutkha is a pre-packaged product, containing chopped areca nut, slaked lime, catechu, spices and powdered tobacco [6]. The mainpuri one of the SLT product, made up of pieces of tobacco leaves, finely cut betel nut and other ingredients, mixed thoroughly with lime. The name of this SLT product is taking from a mainpuri district in the northern state of Uttar Pradesh, where initially this product is prepared and consumed [7]. The dry brown snuff (DB), composed of tobacco ash, cotton or sesame oil. While dry black snuff (DBK) are made from tobacco ash, slaked lime and indigo [8].

Elemental level of tobacco is a function of many factors like soil characteristics, climatic conditions and plant variety [9]. Tobacco plant (*Nicotiana tabacum*) is well known for its capacity to concentrate metals from its growing environment [10,11]. Some metals found in tobacco are essential human nutrients, including iron, copper, chromium and manganese, but high levels of these elements in certain organ systems may contribute to injury of different organs. There has been a recent interest in the role of Cu²⁺, as a possible etiological factor in the development of oral disorder. It was reported that some gradients of SLT products contains high Cu²⁺ content and that during chewing may raise the salivary levels of soluble Cu²⁺ [12]. It has been reported that statistically there is significantly higher concentrations of Cu²⁺ in the blood of tobacco smokers than nonsmokers [13].

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The Cu^{2+} is an essential element for many biological systems in the human body [14]. A daily dietary intake of 1–2 mg of Cu^{2+} seems to be necessary for its dependent metabolic processes in adults [15]. The increased levels of plasma Cu^{2+} have been found in several physiological and pathological disorders [16]. Exposure to high levels of Cu^{2+} results in various changes in the liver tissues that create oxidative damage to membranes and molecules. Lipid peroxidation causes dysfunction in the cell membrane, decreased fluidity, changes ion permeability, inactivation of receptors and enzymes [17]. Since the Cu^{2+} concentration is very low in biological samples, so sensitive analytical techniques are required for its determination. The flame atomic absorption spectrometry (FAAS) is by far the most widely employed technique for analyte determination but it is not sufficiently sensitive for the direct determination of Cu^{2+} in biological/environmental samples due to the complexity of matrix components and low concentration [18]. Therefore, preconcentration and separation of analyte are needed before its determination. Different preconcentration techniques have been achieved for determination of trace and toxic elements in different environmental and biological samples [19,20]. Up to now, many classical sample preparation method including cloud point extraction [21], coprecipitation [22], solid phase extraction [23,24], liquid–liquid microextraction [25] have been developed. Liquid–liquid microextraction is one of the convenient separation and enrichment method [26].

The Liquid–liquid extraction has been used for decades, but this technique is usually time consuming and requires quite bulk quantity of high purity organic solvents. Furthermore the disposal of these used solvents may also create a severe environmental problem. Due to toxicity of organic solvents, substantial interest has been manifested on the usage of room temperature ionic liquids (RTIL) as one of the most applicable solvent, and they are commonly used as a choice of environmentally benign media to replace volatile organic solvents which can be significantly contribute to environmental contamination. The RTIL are also known as “designer solvents” because their properties can be easily customized by chemical modification or simply pairing ionic species that are available in number of variety [27,28].

To apply miniaturizing liquid–liquid microextraction procedure, solvent to aqueous phase ratio is greatly reduced especially in single drop microextraction (SDME) [29]. The basic principle of SDME is the distribution effect of analytes between a microdrop of extraction solvent at the tip of a microsyringe needle and aqueous sample solution. After extracting for a prescribed period of time, microdrop is retracted back into the micro-syringe and transferred to the instrument for further analysis [30]. A great deal of care and highly concise practical handling are required to design SDME. As prolonged extraction time might be required for drop dissolution and have a high incidence of its loss, results into poor accuracy and precision [31–33]. Practical considerations are also important issue by ensuring reproducible and stable positioning of the sample vial and syringe needle, with the help of stands and clamps [34]. To overcome all of the above problems, we introduced an innovative method, non dispersive ionic liquid based microextraction.

According to literature review up till now, very little research has been carried out on the intake of Cu^{2+} from different SLT products by the population of all age group in Pakistan and other Asian countries. The aim of the present work was to combine the non-dispersive ionic liquid based microextraction (ND-IL μ E) with FAAS for the determination of Cu^{2+} in ASE of SLT products (to better understand the SLT users are immediately exposed to analytes). For proposed procedure, a long narrow glass column (100 cm) with small diameter (2–10 mm), which provide more contact area between two solvent system (aqueous and ionic liquid as extractant). There is no need of centrifugation and dispersing in

propose method. For this developed method, ionic liquid and PAN were chosen as the extractant and chelating agent, respectively. The factors influencing the ND-IL μ E efficiency were investigated in detail.

Materials and methods

Study population

A survey was carried out about the chewing habit of gutkha, mainpuri and dry snuff, from people (both genders), age ranged 18–60 years, residents of different cities of Pakistan. Before the start of study, all users were informed about the aim of study, they agreed to participate and signed the form. A questionnaire was administered to them for collecting the details regarding physical data, ethnic origin, health, age, duration and frequency of SLT consumption. This study was approved by the ethics committee of NCEAC, University of Sindh, Pakistan. From the analysis of 665 questionnaires, we found that more than 56% people consumed both mainpuri and gutkha, 32% people consumed only dry snuff (mostly laborers and drivers). About 12% of these participants were also smokers, in addition to consuming different SLT products.

Sampling

Samples of different brands of gutkha ($n = 11$), mainpuri ($n = 12$) and dry snuff ($n = 9$) were collected/bought from the local markets as per their availability and usage by the people of South Eastern Province of Pakistan, during January to December 2013. Samples of the same brand were mixed together to obtain a representative sample of that product. Brand names have not been disclosed in this paper due to legal requirements. Ten composites samples were made by homogenized each SLT products after removing their wrappers. All samples were dried at 80 °C. The dried samples were ground with agate mortar and pestle, sieved through nylon sieves with mesh sizes of 125 μm , and then stored in the labeled sample bottles.

Chemical reagents and glassware

Ultrapure water obtained from ELGA lab water system (Bucks, UK) was used throughout the study. Concentrated nitric acid (65%), hydrogen peroxide (30%) and hydrochloric acid (37%) were obtained from Merck (Darmstadt, Germany). Working standard solutions of Cu^{2+} were prepared immediately before their use, by stepwise dilution of certified standard solution (1000 mg L^{-1}) obtained from Fluka Kamica (Buchs, Switzerland), with 0.2 mol L^{-1} of HNO_3 . The complexing reagent (PAN) were obtained from (Fluka) and prepared by dissolving appropriate amount of these reagents in 10 mL ethanol (Merck) and diluting to 100 mL with 0.01 mol L^{-1} acetic acid. The nonionic surfactant Triton X-114 was obtained from Sigma (St. Louis, MO, USA) and used without further purification. A 1% (v/v) nonionic surfactant solution was prepared by dissolving 1 mL of Triton X-114 (Merck) in 100 mL distilled water. A stock buffer solution was prepared by dissolving appropriate amounts of acetic acid and its sodium salt in ultrapure water, and pH was adjusted with 0.1 mol L^{-1} HNO_3/NaOH . The artificial saliva was prepared according to Macknight-Hane and Chou formula [35,36]. The artificial saliva was made from different salts (Sigma) in g L^{-1} , KCl (0.625), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.166), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.059), K_2HPO_4 (0.804), KH_2PO_4 (0.326), Methyl-*p*-hydroxybenzoate (2.0), sodium carboxymethyl cellulose (10.0) and 2.5 unit mL^{-1} (2500 unit L^{-1}) of α -amylase [36]. All materials and glassware used for Cu^{2+} analysis were kept at 10% HNO_3 for at least 24 h and

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