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Temperature-controlled ionic liquid-based ultrasound-assisted microextraction for preconcentration of trace quantity of cadmium and nickel by using organic ligand in artificial saliva extract of smokeless tobacco products

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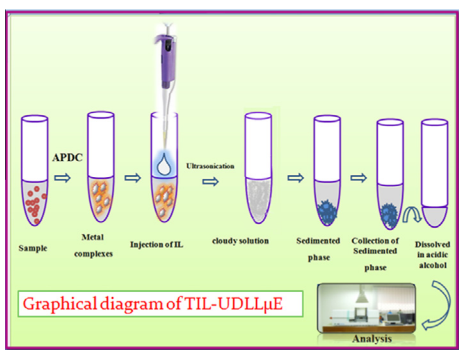
HIGHLIGHTS

- Lack of knowledge about toxic elements (Cd and Ni) in smokeless tobacco (SLT) need to investigate.
- The total and artificial saliva extracted Cd and Ni in SLT products was accomplished.
- The Cd and Ni in artificial saliva extract of SLT immediately available to consumers.
- Long-term use of SLT generates free radicals which promotes the oral cancer.
- APDC using as complexing agent and analyzed by ETAAS.

GRAPHICAL ABSTRACT



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ABSTRACT

A new approach was developed for the preconcentration of cadmium (Cd) and nickel (Ni) in artificial saliva extract of dry snuff (brown and black) products using temperature-controlled ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction (TIL-UDLLμE) followed by electrothermal atomic absorption spectrometry (ETAAS). The Cd and Ni were complexed with ammonium pyrrolidinedithiocarbamate (APDC), extracted in ionic liquid drops, 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6]. The multivariate strategy was applied to estimate the optimum values of experimental variables influence the % recovery of analytes by TIL-UDLLμE method. At optimum experimental conditions, the limit of detection (3s) were 0.05 and 0.14 μg L^{-1} while relative standard deviations (% RSD) were 3.97 and 3.55 for Cd and Ni respectively. After extraction, the enhancement factors (EF) were 87 and 79 for Cd and Ni, respectively. The RSD for six replicates of 10 μg L^{-1} Cd and Ni were 3.97% and 3.55% respectively. To validate the proposed method, certified reference material (CRM) of Virginia tobacco leaves was analyzed, and the determined values of Cd and Ni were in good agreement with

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the certified values. The concentration of Cd and Ni in artificial saliva extracts corresponds to 39–52% and 21–32%, respectively, of the total contents of both elements in dry brown and black snuff products.

Introduction

The tobacco plant (*Nicotiana tabacum*) is widely known for its leaves, which are smoked, chewed, or snuffed in various form. The smokeless tobacco products (SLT) consumed in Western and Asian countries are mostly chewing tobacco and snuff. Although interest is growing in the patterns, distribution, consumption, and compositions of SLT products and its use in various parts of the world [1,2]. Several studies have found that SLT consumption can increase the risk of oral cancer and irreversible gingival recession [3]. Time trends analysis of Pakistan and India have shown an increase in oral cancer among the peoples due to consumption of the SLT products [3,4].

Dry snuff consists of fermented, finely-ground fire cured tobacco that was intended to be placed in the oral cavity. The dry brown Snuff (DB) composed of tobacco, ash, sesame oil. While dry black snuff (DBK), made up of pieces of tobacco leaves, ash, slaked lime and indigo [5]. It is now the most popular form of SLT in the US; where the sales of this product have increased by 77% over the past 15 years [6].

Tobacco plant (*N. tabacum*) is well known for its capacity to concentrate toxic elements from its growing environment. Elemental level of tobacco is a function of many factors like soil characteristics, climatic conditions and plant variety [7]. The international agency for research on cancer (IARC) classified Cd as a human carcinogen [8]. The Cd is highly toxic even at low concentrations, causing damages to organs such as the kidneys, liver, and lungs [9]. The Ni is currently classified as Group 1 "carcinogenic to humans" by the IARC [10]. The Ni has been long known to produce nasal and lung cancers. The Ni, Cd and other heavy metals can also generate free radicals directly from molecular oxygen in a two step process to produce superoxide anion which combine with protons in the dismutation reaction to generating hydrogen peroxide in the process [11,12].

Several advance analytical techniques are available for the determination of trace metals with sufficient sensitivity [13,14]. The analysis of elements in trace levels is a difficult analytical task, mostly due to the complexity of the matrix and the low concentration of these elements, which requires sensitive instrumental techniques and often a preconcentration step [15]. In this regard, a variety of techniques have been proposed for the determination of trace quantity of elements, such as coprecipitation [16,17], liquid–liquid extraction (LLE) [16], cloud-point extraction [18], solid phase extraction [19], and dispersive liquid–liquid microextraction [20], for the separation and preconcentration of Cd and Ni from different matrices. However, these methods often require large amounts of organic solvents, which are mostly harmful and contaminate the environment due to their high vapor pressure. The LLE has been used for decades, but this technique is usually time consuming and requires quite bulk amount of high purity solvents. So microextraction technique, dispersive liquid–liquid microextraction (DLLμE), has been developed for extraction, preconcentration and determination of metal ions and organic compounds [21,22]. The DLLμE is simple, fast and inexpensive, but the required amount of disperser solvent may be high, so it is possible that recoveries decrease proportionately for less hydrophobic species, so a third components are necessary, which usually decreases the partition coefficient of analytes into the extractant solvent [23].

Ionic liquids (ILs) are a class of ionic compounds, which have many unique physicochemical properties such as, low melting points, broad liquid ranges, negligible vapor pressures, good thermal stabilities, non-flammability, and good extractabilities for various organic compounds and metal ions as neutral or charged complexes [24–26]. In temperature-controlled ionic liquid-dispersive liquid-phase microextraction, the IL was dispersed completely into the aqueous solution under the drive of temperature, and the analytes will more easily migrate into the ionic liquid phase [21]. It is well-known that ultrasound is a powerful aid in the acceleration of various steps, such as homogenizing, emulsion forming, and mass transferring between immiscible phases, in the processes of separation and extraction [23]. Ultrasound-assisted liquid–liquid and ultrasound-assisted emulsification extraction have been successfully used as the alternative to LLE, which can attain extraction equilibrium in a short time [27]. However, organic solvents tend to volatilize under the ultrasonic radiation. As a result, providing the advantages of ionic liquid, ultrasound-assisted ionic liquid-based microextraction was developed as a simple, fast, inexpensive, sensitive, and efficient method for extraction [22].

Very little research has been carried out on the intake of Cd and Ni from the dry snuff products (dry brown and black) by the population of all age group in Asian and Western countries. The present study was aimed to investigate the total Cd and Ni concentrations in dry snuff product consumed and available in Pakistan. The dry snuff products was also extracting in artificial saliva to better understand the levels of understudy toxic metals to which consumers are immediately exposed. The aim of the present work was to combine the TIL-UDLLμE with ETAAS for the determination of Ni and Cd in artificial saliva extract of dry snuff samples (brown and black). For this proposed method, $[C_4MIM][PF_6]$ ionic liquid and APDC, were chosen as the extractant and chelating agent, respectively. The variables influencing micro-extraction efficiency such as the volume of $[C_4MIM][PF_6]$, sample pH, temperature, ultrasonic time, concentration of complexing reagent and salt effect were systematically studied by multivariate technique, to evaluated the effects of varying several variables at once. Further optimization was done by a 2^{3+} star central composite design (CCD), which involved 16 experiments.

Materials and methods

Study population

A survey was carried out about the consuming habits of dry snuff, from people (both genders), age ranged 18–60 years, of different cities of Pakistan. Before the start of this study, users were informed about the aim of study, and all agreed to participate and signed the form. A questionnaire was administered to them for collecting the details regarding physical data, ethnic origin, health, duration and frequency of dry snuff consumption, age, and consent. This study was approved by the ethics committee of NCEAC, University of Sindh, Pakistan. From the analysis of 621 questionnaires, we found that more than 54% people consumed both types of dry snuff, 34% people consumed only dry brown (mostly laborers and drivers). About 12% of these participants were also smokers.