

Speciation of inorganic arsenic species and total inorganic arsenic in rice using microwave-assisted dispersive liquid–liquid micro-extraction and electrothermal atomic absorption spectrometry

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Human exposure to inorganic arsenic (iAs) via rice consumption is of increasing concern. In the present study, microwave-assisted dispersive liquid–liquid micro-extraction (MADLLME) and electrothermal atomic absorption spectrometry (ETAAS) were developed for the speciation of iAs in rice samples. After microwave-assisted digestion, the As(III) ion reacted with diethyldithiophosphoric acid (DDTP) to form an As–DDTP complex and was extracted at the same time. Some parameters affecting digestion, complex formation, and extraction were studied and optimised. Under the optimised conditions, a detection limit of $0.2 \mu\text{g kg}^{-1}$ with a correlation coefficient of 0.9901 were obtained with a calibration curve in the range of $0.5\text{--}200 \mu\text{g kg}^{-1}$. Total iAs was determined after reduction of As(V) to As(III) with sodium thiosulfate and potassium iodide, and As(V) was calculated by difference. The proposed extraction procedure was successfully applied for the determination of iAs ions in certified reference materials (NIST CRM 1568a and NMJ CRM 7503a) and 10 rice samples produced in Iran and other Asian countries.

Keywords: inorganic arsenic; speciation; dispersive liquid–liquid micro-extraction; microwave-assisted digestion; rice analysis

Introduction

Arsenic (As) is one of the most toxic trace elements and occurs in both inorganic and organic forms, which are found in the environment from both natural sources and anthropogenic activities. Exposure to As can cause a variety of adverse health effects, including dermal changes, and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects (Mandal & Suzuki 2002). This element occurs in the natural environment in four oxidation states: As(V), As(III), As(0) and As(–III). The mobility and toxicity of As are determined by its oxidation state (Meng et al. 2003). As(III) and As(V) were categorised as being a Group I carcinogen by the IARC (2004). Speciation of inorganic arsenic (iAs) is often as important as total quantification because of its varying degrees of toxicity (Patlolla & Tchounwou 2005). As speciation accumulated in rice is important because rice is a major dietary staple for large populations, especially in Asian countries, and elevated As levels are found in rice and rice products available in the market places around the world (Nishimura et al. 2010; Fu et al. 2011). Therefore, rice consumption is considered to be one of the potential routes of dietary As exposure in many parts of the world (Batista et al. 2011). A combination of iAs, As(III) and As(V) present in rice is an order of magnitude higher than that in wheat and maize, and much higher than that in foods of marine origin (Schoof et al. 1999). The

FAO and WHO have recommended a PTWI of not more than $15 \mu\text{g}$ of iAs kg^{-1} of body weight (Kohlmeyer et al. 2003). Hence, it is important to determine which chemical forms are present in foodstuffs and in the environment and also to analyse the total As concentration (Francesconi & Kuehnelt 2004).

In recent years, many modern instrumental techniques including electrochemical analysis (Song & Swain 2007), electrothermal atomic absorption spectrometry (ETAAS) (Karadjova & Venelinov 2002; Pasiadis et al. 2013), atomic fluorescence spectrometry (AFS) (Yuan et al. 2007), and inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) (Gil et al. 2007; Musil et al. 2014) have been employed for the determination of As(III) and As(V). ETAAS is still being used because it combines a short analysis time, relative simplicity, lower cost, low sample volume requirements and low detection limits.

One of the key and difficult steps in the course of As speciation is the desire to extract As from the rice samples without any disturbance in the origin of As species present (Narukawa et al. 2008; Huang et al. 2012). Sample preparation plays an important role in a whole analytical process to concentrate the target analytes and decrease interferences from sample matrix. A number of pre-treatment methods such as hydride generation (Li et al. 2006, 2009), liquid–liquid extraction (LLE) (Muñoz et al. 1999),

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