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Determination of lead at trace levels in mussel and sea water samples using vortex assisted dispersive liquid-liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry

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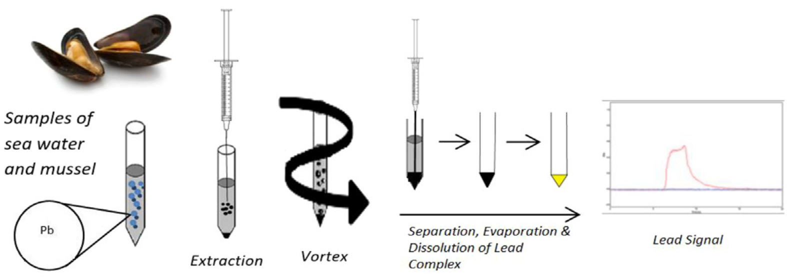
HIGHLIGHTS

- A novel DLLME-SQT-FAAS method was developed for the extraction and determination of lead at trace level.
- The applicability and accuracy of the method was verified with spiked recovery tests.
- Low %RSD values indicated high precision for the extraction process and instrumental measurements.
- The method was applied to mussel and sea water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, dispersive liquid-liquid microextraction (DLLME) and slotted quartz tube (SQT) were coupled to flame atomic absorption spectrometry (FAAS) to increase the sensitivity of lead. Conditions such as the formation of the lead-dithizone complex, efficiency of the DLLME method and the output of the SQT were systematically optimized to improve the detection limit for the analyte. The conventional FAAS system was improved upon by about 3.0 times with SQT-FAAS, 32 times with DLLME-FAAS and 142 times with DLLME-SQT-FAAS. The method was applicable over a wide linear range (10–500 μg L^{-1}). The limit of detection (LOD) determined by DLLME-SQT-FAAS for seawater and mussel were 2.7 μg L^{-1} and 270 μg kg^{-1}, respectively. The percent recoveries obtained for mussel and seawater samples (spiked at 20 and 50 μg L^{-1}) were 95–96% and 98–110%, respectively.

1. Introduction

Lead can be found in the environment from natural sources and man-made activities, and it poses some risks to living organisms and human being such as hematological, cerebral, and kidney malfunctions (Manahan, 1994; Huang and Keller, 2015). At the prenatal development of the brain, lead exposure might cause permanent adverse effects on neurocognitive function resulting in lower mental development and risk of schizophrenia later in life (Opler et al., 2004, 2008; Bellinger, 2013). Plumbism as a disease of lead poisoning has different symptoms such as hyperactivity, developmental delays, hearing loss, and even death (Hauptman

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et al., 2017). Lead can be entered into the human body in the form of inorganic lead and accumulated in soft tissues, bones, and teeth or as organic lead which accumulates in the brain because of its fat-soluble nature (Tchounwou et al., 2012). For this reason, there are several regulations on the release of lead into the environment. However, the automotive, ceramic, ink, pesticide and fertilizer producing industries make use of lead materials resulting in lead contamination (Comitre and Reis, 2005). In addition, lead can be easily transferred into drinking water by means of corrosion and old lead pipes found in several living places (Cartier et al., 2012; Frisbie et al., 2015).

According to the World Health Organization (WHO), the tolerable weekly amount of lead for humans is 25 μg kg^{-1} body weight (Mertz, 1983). In order to control the amount of lead in drinking water, the United States Environmental Protection Agency (USEPA) and WHO have published regulations including maximum levels of lead which are 0.015 and 0.010 mg L^{-1}, respectively (Etchie et al., 2013; Bakırdere et al., 2016). The maximum level of lead recommended for meat and fish by the European Union range between 0.10 and 0.30 μg g^{-1} (EC, 2006). Hence, due to the several health effects, it is crucial to use sensitive analytical methods to determine this element at trace levels in water and food samples. Various techniques such as flame atomic absorption spectrometry (FAAS) (Bakirdere and Yaman, 2008), electrothermal atomic absorption spectrometry (ETAAS) (Cabon, 2002), hydride generation atomic absorption spectrometry (HGAAS) (Bakırdere et al., 2016) and inductively coupled plasma with optical emission spectrometry (ICP-OES) (Koksal, 2002) and mass spectrometry (Søndergaard et al., 2015) detection have been used for the determination of lead in various matrixes.

FAAS has been commonly used due to its simplicity, low cost and operational ease (Santos et al., 2016). However, FAAS is not sensitive enough to obtain very low detection limits for several metals including lead due to low nebulization efficiency (Bakirdere et al., 2011). Hence, preconcentration methods or additional apparatus like a slotted quartz tube can be applied to overcome the sensitivity limitation of this instrument (Özzeybek et al., 2017). Slotted quartz tube developed by Watling in 1977 (Watling, 1977) could be easily fitted onto the flame burner head of FAAS to achieve low detection limits for heavy metals (Ataman, 2008; Demirtas et al., 2015). Residence time of analyte atoms in the flame and interaction between hollow cathode lamp light and metal atoms can be increased with the help of SQT (Kaya and Yaman, 2008; Fırat et al., 2017). In addition, SQTs can be used to trap atoms by coating the inner surface of the tube with metals that have higher melting points than the analyte of interest (Ataman, 2008). Flame furnace atomic absorption spectrometry is another technique which greatly improves the sensitivity over the conventional FAAS due to improved sample introduction systems such as thermospray and chemical vapor generation (Wu et al., 2008, 2009a, 2009b).

Sample preparation and preconcentration methods such as extraction, co-precipitation, solvent evaporation and ion exchange for the determination of metals can be performed to alleviate matrix effects and improve the detection limit (Biparva and Matin, 2012). Microextraction methods are very popular due to their several advantages (Özzeybek et al., 2017). In literature, dispersive liquid-liquid microextraction (DLLME) as one of the microextraction methods has been successfully employed for the determination of polycyclic aromatic hydrocarbons (PAHs) (Rezaee et al., 2006), pesticides and endocrine disruptor compounds (Chormey et al., 2017), and metals (Biparva and Matin, 2012). DLLME has many advantages such as simple application, rapidity, high recovery and enrichment factor (Turan et al., 2017). This extraction method only requires a ternary component solvent system which consists of extraction solvent, dispersive solvent and aqueous sample (Özzeybek et al., 2017). In DLLME method, a mixture of extraction and dispersive solvents is rapidly injected into aqueous solution and phase separation is accelerated by centrifugation. The analyte in the sediment phase can then be determined proper instrumentation (Farajzadeh et al., 2007; Nagaraju and Huang, 2007).

In this study, a novel analytical method was developed for the determination of lead at trace levels. All the system parameters for DLLME-SQT-FAAS method were elaborately optimized to improve the sensitivity of the system. The developed method was applied to sea water and mussel samples to show the suitability of the method for selected matrices.

2. Materials and methods

2.1. Reagents

All the chemicals and reagents used in this study were of analytical grade unless stated otherwise. Stock standard solution of lead with a concentration of 1000 mg L^{-1} was supplied from High Purity Standards. Dithizone (ligand), acetonitrile, 1,2-dichloroethane, sodium chloride, nitric acid (65%), hydrogen peroxide (30%), dichloromethane, isopropyl alcohol, carbon tetrachloride, ethanol, methanol, toluene, hydrochloric acid (37%), disodium hydrogen phosphate, sodium hydroxide, potassium chloride and potassium nitrate were purchased from Merck (Darmstadt, Germany). Ultrapure water from a MilliQ Reference System at the Central Laboratory of Yıldız Technical University was used throughout the experiments with the quality of 18.2 M-ohm-cm.

2.2. Instrumentation

An Analytik Jena AG NovAA 300 atomic absorption spectrometer with a flame burner and deuterium hollow cathode lamp (D_2) was used throughout this study. The burner head of the FAAS was equipped with a lab-made quartz tube having the following dimensions; 16 mm internal diameter, 18 mm external diameter, 14 cm length, 5.5 cm entrance slot and 3.0 cm exit slot. The entrance slot was cut to fit the length of the burner flame which was 5.5 cm. The wavelength of a lead hollow cathode lamp operated at 6.0 mA was 283.3 nm and the monochromator spectral bandpass was 0.50 nm. Digestion of mussel samples was performed with a Milestone microwave digestion system. (see Fig. 1)

2.3. Procedure of DLLME

A volume of 8.0 mL aqueous lead standard/sample solution was added to 0.50 g NaCl in a 15 mL centrifuge tube, after which 1.0 mL phosphate buffer solution (pH 12 and 1.0 mL of ligand solution (dithizone dissolved in ethanol) were added. The resulting solution was vortexed for 4.0 min to disperse the ligand homogeneously throughout the solution for a rapid and complete complexation. A mixture of 1,2-dichloroethane (200 μL) and acetonitrile (2.0 mL) were mixed in a separate tube and injected into the solution including lead-dithizone complex with a syringe. A cloudy solution was formed in the tube and it was mixed by vortex for 15 s. The solution was then centrifuged at 3460 *g* for 2.0 min. After the centrifugation, the settled organic phase at the bottom of the tube was transferred into a clean tube and placed in a water bath (100 °C) for total evaporation. Concentrated nitric acid (150 μL) was added to dissolve the lead complex residue while heating in a water bath. Vapor stemming from the heating process was condensed in a refrigerator and centrifuged in order to settle all droplets at the bottom of the tube.